Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XIII.

PAPERS READ BEFORE THE ACADEMY.

I.

REVISION OF THE ATOMIC WEIGHT OF ANTIMONY.

BY JOSIAH P. COOKE, JR.,
Erving Professor of Chemistry and Mineralogy in Harvard College.

THE first determination of what we now call the atomic weight of antimony was made by Berzelius, and the result published in 1818.* His method consisted in oxidizing the metal with nitric acid and igniting the residue. This product he called antimonious acid; and, after a careful study of the chemical relations of the several oxides and of the native sulphide of antimony, he assigned to antimonious acid the symbol $Sb\,O_4$, that of the basic oxide being $Sb\,O_3$, and of the native sulphide $Sb\,S_3$. In some earlier experiments,† Berzelius had not obtained constant results with the same process, 100 parts of "pure antimony" having yielded in four experiments 125.8, 126, 127.5, and 127.8 parts of antimonious acid respectively; but in his later paper he attributes the discordance to the circumstance that he had previously conducted the process in glass flasks, "which could not bear a sufficiently strong heat to change all the yellow residue into white oxide." By the later experiments, in which platinum vessels were used, he found that 100 parts of antimony yield 124.8 parts of antimonious acid. But although he distinctly states "that when pure antimony is oxidized in a flask with nitric acid, and the mass evaporated to dryness in a platinum crucible is heated until it becomes perfectly white, the same results are always obtained," nevertheless, in the paper cited, he does not give the several determinations on which his conclusion was based, or any details by which we can now judge of the purity of the metal used. He simply gives the single result just cited, from which we readily deduce as the atomic weight of antimony 129; and with this value he appears to have been contented; for we find in his masterly review of the atomic weights of the chemical elements, published in 1826,* the same value given, without further comment, and it remained unquestioned for more than thirty-eight years.

---

* Schweigger Jour. für Chem. und Phys., xxii. 70, 1818.
† Ibid., vi. 149, 1812.

Not until 1856 does any further investigation of the subject appear to have been made. In February of that year, R. Schneider, of Berlin, published a preliminary notice;† and later, in May, the full details‡ of a new determination of the atomic weight of antimony, made by a method wholly different from that of Berzelius. This method consisted in reducing a pure native sulphide of antimony by hydrogen gas. The material selected was the antimony glance of Arnberg, which is distinguished for its high degree of purity, and by appropriate tests the mineral was shown to be free from arsenic and the metals which usually accompany antimony. The only impurity that could be discovered was a small amount of quartz, which is associated with the mineral as gangue; but this was of no importance, since the amount could be determined in every experiment with almost absolute precision. The same was almost equally true of two well-known defects in the process, which, if not allowed for, would become sources of error; namely, the escape in vapor, or, mechanically, of a small amount of sulphide of antimony during the reduction, and the circumstance that a further small amount of sulphide escapes reduction by becoming enclosed in the regulus. The first of these effects would diminish, and the second increase, the weight of the regulus; and the same effects would also respectively diminish or increase the atomic weight of antimony calculated from the observations. The two sources of error evidently tend to balance each other; but, on the other hand, the effect of the last is several times greater than that of the first. The total effect, however, is but small; and, had these known sources of error been wholly overlooked by Schneider, the effect would only have been to raise the mean result about 0.26. So far, however, from neglecting these very small errors, Schneider in every case accurately collected and determined both the sulphide of antimony volatilized and the sulphur retained by the regulus, and with these amounts, never exceeding a few milligrammes, he corrected his observed data. In the paper referred to, Schneider gives the detail of eight separate determinations, the mean of which gives for the atomic weight of antimony the value 120.30, and this differs from the extremes on either side by only 0.23. In this determination, the atomic weight of antimony is referred to that of sulphur, which is taken as 32.*

---

* Poggendorff's Annalen, viii. 23, 1826.

† Ibid., xcvii. 483, February, 1856.

‡ Ibid., xcviii., 293, May, 1856.

In the next number of Poggendorff's "Annalen" to that in which the paper of Schneider appeared, Heinrich Rose published the result of a previous analysis of $Sb\,Cl_3$, made under his direction by Herr Weber, which gives for the atomic weight of antimony the value 120.7 when chlorine is 35.5; and, although we have only the evidence of a single analysis, yet this one was thought by Rose to be of especial value as confirming the subsequent determination of Schneider. This confirmation he regarded as the more satisfactory, since by Weber's analysis the atomic weight of antimony is referred to chlorine, and not as before to sulphur or oxygen. The process was this: A weighed amount of $Sb\,Cl_3$, purified by repeated fractional distillation, was dissolved in an aqueous solution of tartaric acid. From this solution the metal was precipitated by H_2S, and in the filtrate the chlorine was determined by precipitation with $AgNO_3$ in the usual way.

Next in order in this series of investigations comes the admirable work of Mr. W. P. Dexter. He adopted the same process as Berzelius, but conducted it with all the refinement which ingenuity, guided by the increased chemical knowledge of the time, could devise. Especial care was taken to secure pure metallic antimony; and a comparison of the results obtained with different specimens — purified by the processes he describes — shows conclusively that, even if the metal was not absolutely pure, the error resulting from this cause was wholly inappreciable. The agreement between the results of the several experiments is wonderfully close, but for the details we must refer to the original paper.† It is only important to state here that Dexter obtained for the atomic weight of antimony, as the mean of ten determinations, the value 122.34, and that the extremes on either side were

---

* Poggendorff's Annalen, xcviii. 455, June, 1856.

† Ibid., c. 563, April, 1857.

122.24 and 122.48. The difference between these extremes corresponds to only 1 milligramme in 3 grammes of Sb_2O_4, which was about the average amount weighed in these experiments.

In June, 1861, F. Kessler, of Dantzic, published in Poggendorff's "Annalen" a paper * devoted to a re-examination of the atomic weights of chromium, arsenic, and antimony, based on a method of volumetric analysis which he had previously described in the same journal.† Indeed, in his earlier paper he had already quite fully elaborated the subject, and thus anticipated both Schneider and Dexter in correcting the old number of Berzelius. The method of Kessler was based on the reciprocal relations of potassic dichromate and ferrous chloride; and, as is well known, standard solutions of these salts are especially well adapted to volumetric determinations, by the circumstance that the neutral point can be so accurately fixed by the reaction with potassic ferricyanide. For the details of the method, which were quite numerous and complicated, we must refer to the original paper. It is sufficient for the present purpose to say that the atomic weight of antimony was thus indirectly referred to the molecular weight of potassic chlorate, which was taken as 122.57, according to the determinations of Pelouze and of Marignac. Kessler experimented with antimony, with antimonious oxide, and antimonious chloride, and obtained results varying between 121.67 and 122.61. We translate his own commentary: "Although the results of these experiments, taken as a whole, agree very nearly with those obtained by Dexter, I must nevertheless confess that I am not wholly convinced that our number, which is two hydrogen units higher than that found by Schneider, is much nearer the truth than his. Every one who has occupied himself with the analysis of different antimony compounds must be able to indorse what Berzelius wrote in 1812: 'I have never worked with a material with which it was so extremely difficult to obtain constant results.' . . . Nevertheless, I believe I have been able to show that in the analysis of antimony compounds the volumetric method is capable of affording a very sharp control over results obtained in other ways."

Before the Académie des Sciences in Paris, in 1857 and 1858,‡ Dumas read the results of his celebrated revision of the atomic weights of the chemical elements, during which he redetermined the atomic weight of antimony.§ With this, as with most of the other elements

---

* Poggendorff's Annalen, cxiii. 134, June, 1861.

† Ibid., xcv. 204, June, 1855.

‡ The 9th of November, 1857, and the 27th of December, 1858.

§ Annales de Chimie et de Physique, 3me Séries, LV. 175, February, 1859.

whose atomic weights he redetermined, his process consisted in analyzing the chloride ($SbCl_3$) and weighing the chlorine as argentic chloride. The antimonious chloride was prepared by the action of dry chlorine on pure antimony, — "de l'antimoine très-pur et du chlor sec," — and purified by repeated distillations over the metal in fine powder. A weighed amount of this chloride was added to a solution of tartaric acid in water, and the chlorine directly precipitated in the usual way. Dumas adds: "Je n'ai entrevu ni apparence de cause d'erreur particulière, ni irrégularité dans les résultats." He gives four determinations as follows: —

1. 1.876 of $SbCl_3$ correspond to 2.660 Ag; hence Sb = 122.00
2. 4.336 „ „ 6.148 „ „ = 122.00
3. 5.065 „ „ 7.175 „ „ = 122.20
4. 3.475 „ „ 4.930 „ „ = 121.94

The first three were from the same, but the last from a different preparation. From these results, Dumas deduces as the most probable value of the atomic weight of antimony the whole number 122, and this differs from the extreme value obtained by only 0.2. It will be noticed that the method of Dumas is essentially the same as that of Rose, only the former did not separate the antimony from the solution before precipitating with argentic nitrate. This, however, may be an important difference; for, as we shall show hereafter, an excess of argentic nitrate, added to a solution containing antimonious chloride and tartaric acid, above the amount necessary to precipitate the chlorine, determines the formation of argento-antimonious tartrate, which slowly crystallizes out from the solution on standing, and is almost wholly insoluble in cold water. The occlusion of this material by the precipitated argentic chloride on the one hand, and on the other hand the slight solubility which we also noticed of this precipitate in the resulting menstruum, gave us a very different impression of the accuracy of the process from that obtained by Dumas. Rose, however, does not mention these possible sources of error. It seems probable that Weber, under his direction, aimed to estimate the antimony as well as the chlorine of the compound analyzed, and for this reason precipitated the antimony first. Moreover, the chief of the causes of error we have noticed would tend to lower the observed atomic weight of antimony; and our experience would lead us to question whether the previous precipitation of the antimony would not occasion more error than it prevents.

The only other determination of the atomic weight of antimony which has come to our knowledge was made incidentally by B. Unger* while studying the chemical relations of Schlippe's salt, Na_3S_4Sb-9 H_2O. An analysis of this salt gave $Sb = 119.76$, when $S = 32$ and $Na = 23$; but this value rests on a single experimental determination, by a method from which great accuracy could not be expected.

As is well known, the value 122 obtained by Dumas is the one which is almost universally accepted as the atomic weight of antimony, and this not only in consequence of the deservedly great authority of this distinguished experimenter, but also because his result so nearly agrees with the previous determination of Dexter. Nevertheless, a careful examination of the work of Schneider, referred to above, will convince every chemist that it is impossible to refer the difference between 120.3, the number he obtained, and 122, to any experimental errors. This difference is nearly one and a half per cent of the whole value; although it is evident that the probable experimental error does not, in either case, amount to one tenth of one per cent. Moreover, it will be found that this investigation of Schneider is a model of its kind. All the details of the experimental work are given, and it is evident that every precaution was taken which the circumstances required. Furthermore, the method of Schneider has a very great advantage over all the processes by which the atomic weight of antimony has been determined, in that he was able to obtain satisfactory evidence, not only of the purity, but also of the definite atomic composition of the material he analyzed. In the determination of an atomic weight, it is not only essential that the substance selected for analysis should be pure, in the sense of containing no adventitious elements: it is even more important that neither of the constituents whose atomic ratio is to be determined should be present in excess of the normal proportion. But, while experimenters have been most careful to establish the purity of their material in the first sense, they have seldom given a thought to the possibility of such an impurity as the preponderance of one or the other of the proper constituents of the compound practically constitutes. Theoretical considerations, based on the law of definite proportions, might lead a chemist to believe that impurity in the last sense was impossible in a true chemical compound. But how are we to know that a given material is of the true type? It is certain that the ordinary physical tests of purity, such as the melting point and the boiling point, are insufficient; and the same is equally true of the perfection of crystalline form, that character on which of all others the chemist most frequently relies. As early as 1860, we ourselves showed that constancy of crystalline form was, under certain conditions, compatible with quite wide variations of compositions;* and our conclusions have been most fully confirmed by the results of investigations since made, which reveal the great complexity of crystalline structures. In the compounds † of zinc and antimony which we investigated, the variation was large, because the affinity was weak; but we gave abundant evidence that similar variations, although of less extent, are not uncommon in more stable compounds, and from our subsequent experience we feel confident that in proportion as analytical processes become more accurate these variations will become more apparent. At present, they are to a great extent concealed, because the possible errors of our analytical processes are so great; and we very properly refer, at the outset, any seeming variations from exact atomic proportions to errors of this class. But, in the more accurate methods on which we should alone rely for fixing atomic weights, such variations, when they exist, become of great importance. For call by whatever name you please that small portion of either constituent of a compound which may be present in a crystal over and above the atomic ratio, — regard it merely as so much "dirt" entangled by the crystalline structure, —

---

* Archiv. der Pharmacie, 1871, Band 197, S. 194.

---

* Crystalline Form not Necessarily an Indication of Definite Chemical Composition. Philosophical Magazine, June, 1860; also Poggendorff's Annalen, Band cxii. 90; also Memoirs of American Academy of Arts and Sciences, New Series, vol. v. p. 337.

† Rammelsberg has expressed the opinion — Pogg. Ann., cxx. 61, 1863 — that all crystalline alloys are isomorphous mixtures of the constituent metals, and includes under this category the two compounds of zinc and antimony here referred to; but, had this accurate observer repeated our experiments and measurements, he would have seen that the whole order of the phenomena we studied is inconsistent with such an assumption. Although the two metals may be alloyed in all proportions, yet we give in our paper the strongest evidence that the union is attended with definite chemical action, which has two maxima at the points represented by the symbols Sb_2Zn_2 and Sb_2Zn_3; and although the measurements of the two sets of crystals may be referred approximately to the same fundamental form, as is frequently the case in the simpler systems, especially if we admit such ratios as 4:5, yet the two types of crystals differ completely in their habit, and the very remarkable circumstances of their formation prove that they are essentially distinct. For a full statement of these circumstances we must refer to our original paper above cited. In the very partial abstract from this paper — Pogg. Ann., xcvi. 584 — to which Rammelsberg alone refers, none of these important facts were given; and, moreover, Rammelsberg does not seem to have noticed that our paper published in 1855 preceded Schneider's determination of the atomic weight of antimony.

yet so long as it is there, and your analytical processes do not distinguish it from that portion of the same element which is chemically combined, it is obvious that impurity of this kind will vitiate your result to a far greater extent than an equal amount of wholly foreign admixture; and of what use can it be to refine processes or multiply and discuss observations, if so large a door is left open to constant errors? Moreover, it must not be overlooked that such errors, from their very nature, are apt to have a constant value, and are for that very reason the more liable to deceive. In the investigation just referred to, we showed that under constant conditions the composition of the crystals was definite and invariable, although they might contain — as dirt or impurity, very possibly — an excess of one or the other elementary substance when compared with the normal atomic proportion. Assuming, then, such an excess to be present in the substance selected for analysis, it is perfectly evident that a large error might exist in the determination of an atomic weight, although there was a close agreement in the analytical results. Such agreement therefore is in itself no proof of accuracy; and far less sharp results may be more trustworthy, if only it can be shown that the errors are properly distributed. Errors of the last class can be to a great extent eliminated by multiplying observations, while a constant error is only perpetuated thereby.

The special cause of constant error we have been discussing is one we have specially studied, and one therefore which we naturally select to illustrate the principle we have aimed to enforce. It is not, however, the only cause of constant error which tends to change the apparent ratio between the weights of the various elements of a compound, or the one whose influence is most to be feared in the determination of an atomic weight. Our knowledge of the chemical and physical relations of the materials analyzed, or of the circumstances connected with the processes employed, is in many cases as yet so far from perfect that to a certain extent we work as it were in the dark, and are liable to fall into errors from which only more accurate knowledge could protect our results. As will appear in the sequel, this truth has been forced upon us again and again during the course of the present investigation, and it has led us to bestow upon the work an amount of labor which is far greater than the importance of the results would seem to justify. The experience, however, has left with us a strong conviction on two important points; and we shall describe the several steps in our investigation more in detail than might otherwise seem necessary, in order that the reasons of these convictions may appear. In the first place, we are persuaded that in the determination of atomic weights it is just such constant errors as we have encountered that are almost solely to be feared, and that the mechanical perfection of our analytical methods is far in advance of our chemical knowledge of the materials and processes we employ. In the second place, we feel assured that no agreement, however close, of results obtained by the repetition of the same process, under the same conditions, gives any certain guarantee of the correctness of the atomic ratio which is sought to be established; and hence that in the present state of science no certain conclusions can be reached in regard to the validity either of Prout's Law or of other numerical relations between the atomic weights of the chemical elements.

We return now to our former position,— that in determining an atomic weight it is of the first importance to show that the compound analyzed is not only pure in the ordinary sense, but also that it contains the elements to be compared in atomic proportions. And, after carefully reviewing the whole subject in the light of our present knowledge, we have been led to the conclusion that the most satisfactory evidence on this point we can obtain is that furnished by a chemical reaction, in regard to which it can be shown that the two elements under comparison are transferred without loss or elimination of material from one combination to another. Now, satisfactory evidence of this kind may be adduced in regard to the method of determining the atomic weight of antimony employed by Schneider. The native sulphide of antimony which he analyzed dissolves in hydrochloric acid with the evolution of hydric sulphide, leaving no residue saving a minute amount of silicious gangue, which can be accurately estimated. If then sulphur is combined in atomic proportions with hydrogen in the gas evolved during this reaction, it must also have been combined in atomic proportions with antimony in the original compound; for otherwise the metathesis could not have taken place without an elimination of the excess of one or the other of the constituents. To this familiar fact, we can add still other evidence which makes the proof complete. In the first place, we have repeatedly verified the statement of other chemists, that when — as is always the case unless great care is taken — an excess of sulphur is precipitated by the action of hydric sulphide on solutions containing antimony, this excess, however small, is eliminated, and remains undissolved when the dried precipitate of Sb_2S_3 is dissolved in pure hydrochloric acid. In the second place, during our investigation of the zinc and antimony compounds above referred to, we prepared artificial crystals of antimony glance containing several per cent of antimony in excess of the normal proportion. These crystals were made by fusing the native mineral with an excess of metallic antimony, and pouring out the still melted mass from the crucible, after a portion had crystallized. But although the crystals were extremely brilliant, and had at least this outward characteristic of a definite compound, yet, when dissolved in hydrochloric acid out of contact with the air,* the excess of metal was left undissolved in the condition of a fine powder.

For the reasons we have stated, we have always had great confidence in the results of Schneider, while on the other hand we have felt that both in the case of the oxide of antimony weighed by Dexter, and the chloride of antimony used by Dumas, we could not from the nature of the case have any satisfactory evidence that the material analyzed had the exact atomic composition assigned to it. The antimonic oxide is a perfectly amorphous and inert powder, in regard to which we have neither the evidence of physical properties nor of chemical reactions on the point in question. Moreover, our knowledge of the circumstances under which it is formed would lead us to suspect an admixture of a lower oxide in the product, which would be protected from oxidation (during the ignition) by the surrounding mass, and protected to the same degree under the same conditions. Again, in SbO_2 the weight of the oxygen is only about one-fourth of that of the antimony, so that a very small variation in the weight found would make, in the result, all the difference which is in question. In chloride of antimony, on the other hand, the amount of chlorine is nearly equal to that of the antimony; and for this reason, as well as because chlorine can be so accurately determined, this substance would seem at first sight to be the best adapted of all others for determining the atomic weight of antimony. Our experience, however, has not confirmed this first impression; for although we have found no difficulty whatever in obtaining the material beautifully crystallized and free from such impurities as we should ordinarily look for, yet it is so wonderfully hygroscopic and liable to alteration that we have not as yet succeeded in preparing it for analysis under such conditions that we could feel assured that it was wholly free from moisture or the resulting oxichloride of antimony; and although with sufficient labor and ingenuity the difficulties in the way could undoubtedly be overcome, yet a substance which must be guarded with such precautions is not the best adapted for determining an atomic weight. When, therefore, we had devised the method of precipitating metallic sulphides, described in the previous volume of this series,* and found that by its means, and also by boiling the liquid, as suggested by Mr. S. P. Sharples,† we could precipitate sulphide of antimony in a condition apparently peculiarly well adapted for accurate determination, we conceived the idea of reversing Schneider's method, and verifying his result by a synthesis of the same material which he analyzed. The event, however, proved that we had undertaken a work of far more difficulty than we anticipated. We have met unforeseen obstacles at almost every step of our investigation, and have had constant occasion to indorse, with Kessler, the opinion of Berzelius quoted above.

---

* Antimony is wholly insoluble in hydrochloric acid out of contact with the air.

In the preparation of pure metallic antimony, we were greatly guided by the experience of Mr. Dexter; ‡ and our several products must have been very similar to his, as the following determinations of the specific gravities of the different buttons show. The observed values were reduced to 4° C., on the assumption that the coefficient of cubic expansion for antimony between 0° and 100° C. is for each degree 0.000033, as observed by Kopp. The letters here given will be used throughout the table to designate the various specimens. As might be supposed, the specimens were prepared at different times and at different stages of the investigation, but the results are united here for the convenience of comparison and of reference.

SPECIFIC GRAVITIES OF BUTTONS OF PURE METALLIC ANTIMONY.

Observations of J. P. C., Jr.		Observations of W. Dexter.	
A	6.7025	b	6.7087
B	6.7036	c	6.7026
C	6.6957	c	6.6987
D	6.7070	d	6.7102
E	6.7022	e	6.7047
F	6.7023	e	6.7052
Mean	6.7022	Mean	6.7050

---

* On a New Mode of Manipulating Hydric Sulphide, vol. xii. of these Proceedings, p. 113.

† American Journal of Science and Arts, Second Series, vol. l. p. 248.

‡ Poggendorff's Annalen, Band 100, Seite 564 (*loc. cit.*).

Specimen A was prepared from potassic antimoniate (marked Robiquet and Pelletier, *pur*). A solution of the salt in water was filtered into a similar hot solution of sodic carbonate. The precipitated sodic antimoniate was thoroughly washed with hot water, then dried, and reduced with potassic cyanide. Lastly, the regulus was remelted, and kept in fusion for several hours under its own oxide. Specimen B was prepared, in a similar way, from potassic antimoniate (marked Rousseau Frères, *pur*). Specimen C was prepared from commercial antimony. The metal was first oxidized, and the oxide boiled with an excess of pure nitric acid. The oxide was afterwards repeatedly washed with boiling water, and, when dried, was reduced with potassic cyanide. A third of the resulting metal was again oxidized with nitric acid; and this oxide having been first mixed with the rest of the metal, previously pulverized, the mixture was kept melted for a long time in a covered crucible. The purified metal thus obtained was again fused in a porcelain crucible, under its own oxide, for several hours. Specimen D was the residue of C, — part having been used for casting bullets, — again fused for several hours under its own oxide. Specimen E was prepared by the process described above from potassic antimoniate, made by ourselves from commercial antimony. It was fused for four hours under its own oxide. Specimen F was prepared by Liebig's well-known process, and further purified by fusing the regulus for twenty-nine hours under its own oxide. It is unnecessary to add that these fusions were all made in porcelain crucibles, and that only the purest reagents were employed in the various processes, except only in the early stages of the preparation of C and F. These last preparations were both used for casting the antimony bullets with which the solutions of the metal were reduced before precipitating with H_2S, as will be described hereafter.

We give, in a parallel column with our own results, the specific gravities, determined by Mr. Dexter, of the specimens of pure antimony prepared by him, and used in his determinations of the atomic weight of this element. It will be noticed that the agreement is very close, the mean of his results not differing from that of ours as much by one-half as either set differ among themselves. These differences are evidently owing to slight variations in homogeneity, due to the crystalline structure of the metal. This is made probable by the following results which we obtained with specimen F, prepared as described above by Liebig's process. This was repeatedly fused in its own oxide, and the specific gravity taken at each stage of the process.

Specific Gravity of Specimen F.

After five hours' fusion, additional . . .	6.7050
„ „ „ „ „ . . .	6.6977
„ „ „ „ „ . . .	6.6959
„ „ „ „ „ . . .	6.6840
„ nine „ „ „ . . .	6.7022
„ several „ „ „ . . .	6.7012

Such irregular variations as these could obviously not be referred to a gradual change in the purity or composition of the metal.

Of the several processes employed for purifying antimony, the last is the easiest, yields the largest product, and is as effectual as either of the other two. The long fusion of the metal under its own oxide can in no case be avoided, as this is the only sure method of removing the last traces of iron, at least so far as our experience extends. In repeating the work, however, we should prefer to start from antimonious chloride, prepared from antimony glance. This can easily be purified by repeated distillation, and is absolutely free from arsenic, which cannot always be said of the metal obtained by Liebig's process.

To bring a *given quantity* of antimony into solution, so that the whole shall be left in its condition of lowest quantivalence, and therefore be precipitated by H_2S as antimonious sulphide, without the least excess of sulphur, we found to be a very difficult task; nor have we succeeded invariably in effecting this result, except by the indirect method hereafter described. Finely powdered antimony dissolves readily when digested with a concentrated solution of tartaric acid, to which a few drops of nitric acid have been added; but from such a solution, even after the remaining nitric acid has been carefully neutralized, free sulphur is always precipitated with the sulphide of antimony; and, although we tried various ways, we were unable to find any process by which this effect could be wholly prevented. Very singularly we obtained the best results by acting on antimony directly with nitric acid, under such regulated conditions that the metal was wholly converted into antimonious nitrate, and subsequently removing the excess of acid by slow evaporation at a temperature below 100° C. If the conversion is successfully accomplished, then, on adding to the crystalline residue a strong solution of tartaric acid, this residue is at once dissolved, giving a perfectly clear solution, in which the metal is almost wholly, if not entirely, in its lower condition of quantivalence. The difficulty consists in regulating the action of the nitric acid. We succeeded best by using acid of the sp. gr. 1.35, which we added in large excess to the powdered antimony, previously moistened with water, and as soon as, on gently heating the beaker, the action began, we kept the mass in constant agitation, so as to prevent the temperature from rising too high at any point. If during this reaction, or during the subsequent evaporation of the excess of acid, the dry nitrate is heated even to 100°, decomposition ensues, and higher oxides are formed, which are insoluble in tartaric acid. Indeed, this is probably the order of the change even during the violent action of nitric acid on antimony, when antimonic oxide, Sb_2O_4, is the chief product, antimonious nitrate being in all cases formed first, and subsequently decomposed. Unfortunately, we could not always succeed in obtaining a clear solution in this way ; and the loss of pure material occasioned by the unsuccessful trials was so considerable that we soon abandoned the method. Still, it was capable of yielding good results, as the determinations given below will show.

The rest of the process was as follows: The tartaric acid solution having been brought to the proper degree of dilution, — about 250 cubic centimetres to each gramme of antimony, — the free acid was first carefully neutralized with pure caustic soda. A small amount of hydrochloric acid was next added, and the antimony precipitated with H_2S. In these, as well as in all the subsequent determinations, the precipitation was conducted thus: The solution having been made in a large Erlenmeyer flask, and this firmly supported over a gas lamp, a current of washed carbonic dioxide gas was conducted into the liquid from a suitable generator, the glass tube conducting the gas reaching to the bottom of the flask, so that the gas might bubble up through the whole column of liquid. The atmospheric air having been thus completely expelled, then, through a second glass tube similarly arranged, an excess of a supersaturated solution of H_2S was drawn into the vessel from the fountain or siphon described in the paper above referred to. The temperature of the mass was now slowly raised to the boiling point, and the liquid actually boiled for ten or fifteen minutes. The current of carbonic dioxide, continually passing meanwhile, not only excluded the air, but kept the mass in constant agitation and prevented "bumping."

The precipitate thus forms in a granular condition excellently well adapted to bear without alteration the processes of washing and filtering which follow. It does not adhere to the tubes or sides of the flask, and unless there is some oxidizing agent in the solution it does not contain the least trace of free sulphur. The precipitate was washed with boiling water, and as it settles rapidly and quite compactly it was easily washed in the same flask in which the solution was made and the precipitate formed. The precipitate usually occupied about one-tenth of the volume of the flask, and after drawing off the filtrate our rule was to fill the flask five times with boiling water. We were sometimes troubled by the breaking up of the precipitate and the washing of it through the filter, under such prolonged treatment. As is well known, this can easily be prevented by acidifying the wash water, however slightly, with hydrochloric acid, or by an excess of H_2S; but as the last was liable to oxidation, and the first still more objectionable, for reasons which will soon appear, we employed for the same purpose a solution of carbonic dioxide, and this, as we found, effectually prevented the disintegration. If by not settling promptly the precipitate showed any signs of breaking up, we passed a current of CO_2 through the hot water before it was used in the last one or two washings.

In all the later determinations we collected and dried the precipitate in a large platinum crucible by the method of reverse filtering illustrated and described at length on page 124 of the previous volume of these "Proceedings." But, in the two determinations made by the method just described, the precipitate was collected and dried on the porous earthenware filtering cones described by Prof. C. E. Munroe.* The cones with the precipitate were first dried at 100°, and then heated to 220° C. in an atmosphere of carbonic dioxide. Between 210° and 220°, depending somewhat on its condition, the red sulphide of antimony changes suddenly into the gray modification, and in this last condition the product was weighed. In each of these two determinations, on dissolving the gray sulphide in boiling hydrochloric acid, out of contact with the air, a considerable quantity of black residue was obtained. This contained only a very small amount of free sulphur, but consisted chiefly † of carbon, resulting from the charring of the small quantity of tartaric acid, which, as we find, sulphide of antimony invariably carries down with it when precipitated under the conditions here described, and which cannot be removed by any amount of subsequent washing. This charring takes place at the moment when the red is converted into the gray sulphide, and is undoubtedly caused by the heat evolved during this process. That at this point the charring is perfect, and that after the conversion no tartaric acid is left undecomposed, we have proved by several times heating the resulting gray sulphide to 300°, and ascertaining that it underwent no additional loss of weight. As is well known, small quantities of tartaric acid are completely decomposed at this last temperature.* In the two determinations we are discussing, the carbonaceous residue was collected on a weighed filter, and its weight subtracted from the total weight of the dried precipitate. All the remainder was pure Sb_2S_3; and, from its weight and that of the antimony used, the ratio between the atomic weight of sulphur and that of antimony was very easily calculated. The results were as follows: —

---

* American Journal of Science, May, 1871.

† In our preliminary experiments, traces of both lead and copper appeared in this residue, which we traced at once to the tartaric acid "*purissimum*" used, and we found it impossible to procure from chemical dealers tartaric acid free from these impurities. We were obliged, therefore, to purify ourselves all the acid we employed.

FIRST DETERMINATION.

Weight of antimony taken	2.0554	grammes.
Weight of precipitate dried at 240° . .	2.8878	„
„ carbonaceous residue. . . .	.0147	„
„ Sb_2S_3	2.8731	„
„ antimony as above	2.0554	„
Corresponding weight of sulphur . . .	0.8177	„
Hence when $S = 32$, then $Sb =$ . .	120.6	„

SECOND DETERMINATION.

Weight of antimony taken	2.0346	grammes.
Weight of precipitate dried at 240° . .	2.8513	„
„ carbonaceous residue . . .	0.0073	„
„ Sb_2S_3	2.8440	„
„ antimony as above	2.0346	„
Corresponding weight of sulphur . . .	0.8094	„
Hence when $S = 32$, then $Sb =$ . .	120.6	„

It is evident that these results, so far as they go, very greatly tend to confirm the value $Sb = 120.3$ obtained by Schneider; and, in the light of the knowledge we have since obtained, the reason that our first results were somewhat higher than his is perfectly evident. Whenever sulphide of antimony is precipitated under the conditions we have described, it always carries down with it, not only a small amount of tartaric acid, but also a very appreciable quantity of oxichloride of antimony, $SbOCl$, which, like the impurity first named, cannot be removed by washing the precipitate. The molecular weight of $SbOCl$ (171.5) differs but slightly from the *equivalent* weight of Sb_2S_3 (168), so that, were the precipitate dried at 100°, a small admixture of this compound would not sensibly affect the total weight. But, as soon as the temperature reaches 170°, this oxichloride begins to be decomposed, $SbCl_3$ volatilizes, and the more stable oxichloride $Sb_4O_5Cl_2$ is formed. At a low red heat, this last compound is also in its turn decomposed, still more $SbCl_3$ escapes in vapor, and the final residue is antimonious oxide in a crystalline condition. These changes may be represented thus: —

---

* Gmelin's Handbook of Chemistry, Cavendish Edition, vol. x. p. 209.

$$\text{1st.} \quad 5\ SbOCl = Sb_4O_5Cl_2 + SbCl_3.$$

$$\text{2d.} \quad 3\ Sb_4O_5Cl_2 = 5\ Sb_2O_3 + 2\ SbCl_3.$$

At least, these are the reactions when $SbOCl$ is heated by itself in an atmosphere of CO_2, as we shall show further on in this paper. In the presence of a large mass of Sb_2S_3, containing also a trace of organic matter, these effects are undoubtedly somewhat modified and have not been exactly traced. But whenever a precipitate of Sb_2S_3 formed as we have described is heated much above 150°, it yields a white sublimate; and this sublimate, which we have repeatedly tested, consists chiefly of antimony. At times it was pure chloride of antimony which crystallized on the walls of the glass tube used in the experiment; but, when very small in amount, the sublimate was an amorphous white powder, which appeared like oxichloride of antimony, and which may have been formed by the action of a minute quantity of chloride of antimony on the products of the decomposition of the equally small amount of tartaric acid also occluded by the precipitate. It has long been known that precipitated sulphide of antimony dried at 100° loses weight when heated to a higher temperature, and it has generally been assumed that this loss was due to hygroscopic water. But red sulphide of antimony, when precipitated as we have described, is not in the least hygroscopic and can be dried perfectly at 100°. At least, we have never been able to obtain evidence that, after being thoroughly dried at this temperature, it ever contains water as such; and we are confident that the loss of weight is due solely to the causes we have assigned. At the time the first two determinations were made, these facts were not known, and no allowance was made for the loss of chloride of antimony which must have been incurred. This loss fully accounts for the difference between the value we obtained, 120.6, and 120.3, that of Schneider.

It was at this stage of the investigation that we presented a preliminary notice of our results to the American Academy of Arts and Sciences, at the meeting of June 10, 1873. After this, the work was interrupted for more than two years, and was not resumed until the autumn of 1875. Meanwhile, we had perfected the process of reverse filtering above referred to, and devised a more certain, although indirect method of bringing into solution, in its lower condition of quantivalence, a known weight of antimony. This last consisted, firstly, in dissolving a weighed portion of antimony in hydrochloric acid with the least possible addition of nitric acid; secondly, in reducing the solution thus obtained, by boiling it over bullets of pure antimony, determining from the loss of weight of the bullets the amount of metal dissolved. Evidently, the mass originally taken, plus the amount dissolved from the bullets, gave the weight of antimony used in each determination. Several important facts were observed in connection with each of these steps.

1st. It is usually stated that antimony is only very slightly acted on by pure hydrochloric acid, even when concentrated and boiling, but that it readily dissolves on the addition of only a very small amount of nitric acid.* We found that, when wholly protected from the air or oxidizing agents, pure antimony not only does not decompose pure hydrochloric acid, but also that in contact with the air the smallest amount of nitric acid will determine the solution of an indefinite amount of the metal. Assuming that the product of the reduction of the nitric acid is wholly NO, and therefore that the smallest amount theoretically required for the reaction would be represented by the expression, —

$$Sb + (3HCl + HNO_3 + Aq) = (SbCl_3 + 2\ H_2O + Aq) + NO,$$

then 40 parts of antimony would require, in addition to an abundant supply of hydrochloric acid, 21 parts of HNO_3 for its complete solution. The pure nitric acid which we used had a specific gravity of 1.355, and contained therefore about 54% of HNO_3. The same acid diluted with nine times its volume of water, to form what we will call the decim acid, contains only 5.4% of HNO_3; and hence one gramme of antimony, according to our reaction, ought not to dissolve, if less than 10 cubic centimetres of this decim acid were used. Now, in one experiment, of which we have the details on record, 5 grammes of finely powdered antimony were treated in an open flask with 50 cubic centimetres of strong and pure hydrochloric acid, and to this only 1 cubic centimetre of the decim acid was added. The flask was placed in a warm place (30° C.), and frequently shaken. After a short time, the acid became colored reddish-yellow, and the chemical action began. As soon as it ceased, the materials in the flask were shaken together, when the solution became as colorless as water. But on standing in the air the color rapidly returned, and we observed that it always spread from the surface of the liquid downwards. These phenomena were repeated again and again, until after many days the whole of the antimony dissolved. According to our reaction, the 5 grammes of metal should have required 50 cubic centimetres of acid, so that the effect was obtained with only one-fiftieth of the amount indicated by this theory. The action is probably due to the NO, which remains in solution, and in conjunction with the oxygen of the air decomposes the hydrochloric acid, perhaps thus, —

---

* Author's Chemical Philosophy, p. 265.

$$2\ NO + 4\ HCl + O_2 = 2\ NOCl_2 + 2\ H_2O,$$

then

$$Sb_2 + 3\ NOCl_2 = 2\ SbCl_3 + 3\ NO;$$

and afterwards these reactions are repeated indefinitely. But, whether they represent the precise order of the chemical changes or not, there is no question that here, as in the complex reactions of the sulphuric acid chambers, the nitric acid or its products acts as a carrier, and that the oxygen which combines with the hydrogen of the hydrochloric acid comes chiefly from the atmosphere. In practice, we usually used, for dissolving 2 grammes of antimony, 30 cubic centimetres of strong hydrochloric acid and 5 cubic centimetres of the decim nitric acid; and, although this is only one-fourth of the amount of nitric acid required by the formula generally accepted, it is sufficient to determine a very energetic chemical action, during which a large part of the nitric oxide escapes. The action does not generally come on for some time (fifteen or twenty minutes), although it can be hastened by placing the flask in a warm place. But otherwise we did not heat the acid until almost the whole of the antimony was dissolved. When only a few centigrammes of metal remained undissolved, we connected the flask with a reversed Liebig's condenser and raised the contents to the boiling point. The effect of this was to arrest the chemical action by driving off the nitric oxide; and, if the point was rightly chosen, the small residue of antimony, in passing into solution, would reduce almost all of the higher chloride of antimony which had been previously formed. We found it better, however, that some of the higher chloride should be left unreduced rather than that the least trace of antimony should remain undissolved. In the last case, it was necessary to add additional nitric acid, which made trouble at the next stage of the process; and the fact repeatedly observed, that under these circumstances a few milligrammes of antimony will not dissolve in a large excess of hydrochloric acid, even after prolonged boiling, is a sufficient proof of the statement made above,—that pure antimony will not decompose pure hydrochloric acid, unless some oxidizing agent is also present.

2d. Having thus brought a weighed amount of antimony into solution, so that almost the whole was in the condition of antimonious chloride, we completed the reduction by boiling the acid solution over bullets of pure antimony. These bullets were cast in a bullet-mould, and afterwards turned in a lathe, so as to secure a perfectly clean, smooth, and compact surface. Two or three of them were next weighed together in a platinum tunnel, supported vertically by a light glass stand, on the pan of the balance. From the tunnel they were transferred one by one, without touching with the fingers, to the flask containing the solution of antimony made as just described. The flask was then again connected with the reverse condenser, and the liquid boiled; while through a second opening in the cork a slow current of carbonic dioxide was caused to flow through the apparatus. The boiling was continued until the reduction was complete, and the point was indicated by the circumstance that, when it is reached, the solution, at first having a light straw color, becomes perfectly colorless. The original color is caused by the presence of an exceedingly minute amount of iron, which it is almost impossible to keep out of the solution. Indeed, the very dust of the atmosphere will impart enough for the purpose; and this color under these conditions is as delicate a test for iron as that caused by potassic sulphocyanide. It served here as a very useful indicator, but it was no sign whatever of any appreciable amount of impurity, either in the metal or the acid. Another indicator which can be used, although not nearly so conveniently, is the well-known solution of potassic iodide in starch paste, the acid solution of chloride of antimony giving with this reagent the familiar blue color before, but not after, it has been reduced.

It has long been known that the vapor from a boiling solution of antimony in hydrochloric acid carries off a portion of the chloride of antimony. We have found that this is true only when the solution is quite concentrated: that the amount which escapes rapidly diminishes as the solution is diluted, and that it soon becomes wholly imperceptible. Still, as in our experiments the boiling was frequently greatly prolonged, we guarded against any loss from this cause by using the reversed condenser, as above described. The time required for the reduction varied very greatly under different conditions. It was seldom finished in less than an hour, and the process frequently required several hours. The boiling was stopped as soon as the pale color of the solution was perfectly discharged; but, while the flask was cooling, the current of carbonic dioxide was steadily maintained. When cold, a measured portion of a concentrated solution of tartaric acid (containing generally from ten to fifteen grammes of the crystallized acid) was added to the flask, and the contents were then at once transferred to the large Erlenmeyer flask in which the antimony was to be precipitated. The transfer was accomplished very easily and perfectly in the following way.

Into the Erlenmeyer flask was first poured about 500 cubic centimetres of water strongly charged with carbonic dioxide; and then the platinum tunnel, on which, as we have stated, the antimony bullets had been weighed, and which had been carefully protected meanwhile, was placed in the mouth of the large flask. As the solution was now poured in from the smaller vessel, the bullets were of course caught by the tunnel, and the aërated wash water, which also passed through the tunnel, served to wash the bullets as well as the glass. The tunnel and its contents were then dried and weighed, and the loss from the previous weight gave accurately the amount of additional metal which had passed into solution during the process of reduction. It will be noticed that, during the whole process, the balls were never touched with the fingers, or brought in contact with any object by which their weight could be in the least altered. It was found however, to be essential to the success of the method that not more than a few decigrammes of metal, at most, should be dissolved from the balls; for, otherwise, the surfaces became disintegrated, and liable to abrasion. Hence, the objection to using an excess of nitric acid in dissolving the original quantity of antimony.

The precautions here described may seem unnecessary to those who are not familiar with the fact that a solution of antimony in hydrochloric acid oxidizes with very great rapidity in the air, — fully as rapidly as the solution of a ferrous salt. A solution reduced as we have described, which has at first no action on the iodized starch paste, will strike the blue color after it has been exposed to the air for only a few minutes. This property of an acid solution of antimonious chloride is mentioned by Dexter, in the paper already referred to, but we were wholly surprised by the energy of the action. By means of it, antimony can be dissolved in hydrochloric acid without the aid of nitric acid, or of any other oxidizing agent save the air, if only a certain amount of antimonious chloride has once been formed. When, after exposure to the air, the solution is boiled over pulverized antimony, the solution is reduced, and a further portion of the metal enters into solution. After a second exposure, the same process can be repeated, and so on indefinitely. The process is very slow and tedious, but, in one experiment, we succeeded in bringing into solution in this way several grammes of antimony.

The method of precipitating the antimony after the solution was thus prepared has already been described (page 14). It is important, however, to add a few additional facts, which we observed in regard to the two impurities which the precipitated sulphide of antimony occludes; namely, tartaric acid and oxichloride of antimony. In the first place, we found that the relative amounts of these occlusions might be varied indefinitely by changing the relative proportions of tartaric and hydrochloric acids in the solution in which the precipitate was formed. As is well known, the antimony cannot be kept in solution without a certain excess of one or of both of these reagents. In proportion as the amount of one is diminished, that of the other must be increased; and we made a series of experiments to determine what were the minimum quantities required under different conditions. We made determinations in which the antimony was held in solution by hydrochloric acid only; and we found that, in that case, as much as one part of strong acid was required to five parts of water. We thus, of course, wholly avoided the occlusion of tartaric acid; but the amount of oxichloride carried down was so great that the results were worthless. On the other hand, in some more recent analyses, in which we began with pure chloride of antimony, we used only tartaric acid, and, in this case, although the carbonaceous residue was at times large, there was no loss by sublimation. Of the two occlusions, the tartaric acid is by far the least objectionable. This, as we have seen,* is wholly charred when the red sulphide of antimony is converted into the gray modifications, and the carbonaceous residue can be exactly estimated. In the case of the oxichloride of antimony, on the other hand, it is impossible to obtain any satisfactory control either over the chloride of antimony which escapes or the oxide which is left behind. Unfortunately, in starting from metallic antimony, we cannot avoid a large excess of hydrochloric acid in the solution, and must therefore expect more or less oxichloride of antimony in the precipitate. Assuming therefore that 15 cubic centimetres of strong hydrochloric acid were taken to dissolve every gramme of antimony, which was as little as could conveniently be used (but from this the greater part of the HCl gas was expelled during the subsequent boiling), it became, in the second place, an object to determine how much tartaric acid was required to hold the antimony in solution, and to reduce to a minimum the occlusion of oxichloride of antimony by the precipitated sulphide. With this view the following experiments were made. Four solutions were prepared by dissolving in each case 2 grammes of antimony in 30 cubic centimetres of hydrochloric acid, and reducing the solution as above described. To the first of these were added 5 grammes of tartaric acid, to the second 7 grammes, to the third 10 grammes, and to the fourth 20 grammes. They were then each diluted with water to one litre. In the first, oxichloride of antimony was precipitated at once. The other three remained clear; but, in the second and third, crystals of oxichloride formed on standing over night, and in the inverse proportion to the amount of tartaric acid added. On subsequently heating to boiling, the same crystals were precipitated even in the last, and the amount in the others very greatly increased. This crystalline precipitate formed as the solution was heated, and was deposited like acid tartrate of potassium wherever the glass rod touched the sides of the flask. From the first and second solutions almost the whole of the antimony was thus separated.

---

* Page 15.

These crystals were analyzed, and found to be the oxichloride $Sb_4O_5Cl_2$. They will be described in a future paper. It is evident from these experiments that, under the conditions we have given,* from 5 to 10 grammes of tartaric acid to each gramme of antimony are required to prevent the formation of oxichloride of antimony, even in a cold solution; and our experience shows that, even with the larger amount, a perceptible although very small quantity of oxichloride is occluded by the precipitate formed with hydric sulphide. Moreover, our experience indicates that, with an intermediate amount, the loss and gain resulting from the causes we have mentioned are more or less closely balanced. By preserving as nearly as possible identical conditions, and taking, for example, to every 2 grammes of antimony 30 cubic centimetres of hydrochloric acid and 15 grammes of tartaric acid, it was found possible to obtain results closely agreeing not only with each other, but also with what we finally concluded was the most probable value of the atomic weight of antimony. But, during the investigation by which these facts were developed, we made many determinations with varying proportions both of hydrochloric and tartaric acid, in which the error arising from an excess of one or the other must have had its full effect. All these determinations not obviously defective are recorded below; and although a closer agreement would appear, were only those determinations selected which were made after the more accurate knowledge was obtained, and therefore under more favorable conditions, yet we feel much greater confidence in the result obtained by taking the mean of all, since in this mean the errors must be to a great extent, if not perfectly, balanced.

---

* In solutions of the same strength which have not been perfectly reduced, although containing but little of the higher chloride, the oxichloride does not appear to form nearly so readily; but we have made no quantitative experiments on this point.

We were for some time in doubt in what condition the sulphide of antimony ought to be weighed, in order to obtain the most accurate results. Our final judgment was that the errors already referred to would best be balanced, while others would be avoided, by weighing the sulphide, after it had been dried, at from 180° to 200°, but before it was actually converted into the gray sulphide. This conversion takes place between 210° and 220°, varying to that extent in different cases. The change, as we infer, is attended with a sudden evolution of heat, and the action is quite violent. Small particles of the material are frequently projected from the vessel, and we sometimes noticed that the surface of the platinum nacelle became coated with the familiar sublimate of sulphide of antimony. If there was oxichloride in the precipitate, there may be an additional volatilization of chloride of antimony at this time; but the main loss, as we have constantly observed, takes place before the point of conversion is reached. We therefore concluded that more trustworthy results could be deduced from the weight of the red sulphide dried, as we have described, than from that of the gray; and, as will be seen, this judgment was fully confirmed by subsequent experiments on the haloid compounds. We have, however, in all but two instances weighed the sulphide in both conditions, and we give the results of both weighings; and on comparing these results in determinations 8 to 13 inclusive of the table on pages 36–7, which were made under the nearly identical conditions we have above indicated, it will be seen that the differences are far smaller with the red sulphide than with the gray, which shows conclusively that additional causes of error must have affected the last weights, — another circumstance which sustains our judgment.

In the first twelve determinations we did not estimate the amount of the carbonaceous residue, which is assumed to be balanced by the loss of chloride of antimony, although we always tested the purity of the sulphide of antimony by dissolving it in hydrochloric acid, as described. In determination numbered 13, by some chance concurrence of favorable conditions, we succeeded in precipitating the antimony without the usual occlusion of oxichloride, although we used a large excess of hydrochloric as well as of tartaric acid. In this case, there was no evidence of sublimation nor loss during conversion, but a proportionally large carbonaceous residue, which was deducted from the weight of the sulphide; and the result of this determination, as will be seen, still further corroborates our conclusion. The same is true of some analyses of chloride of antimony made more recently, in which we dissolved crystallized chloride of antimony in a concentrated aqueous solution of tartaric acid, without using any excess of hydrochloric acid. In these cases also, the drying of the precipitate, and the conversion from the red to the gray modification, were attended with no appearance of sublimation. Were we to repeat the investigation with our present knowledge, we should follow the indications of these last analyses; and instead of attempting to make the two chief errors as small as possible, and balance them, we should seek to remove from the solution all the free hydrochloric acid, and thus eliminate the error due to the occlusion of oxichloride.* It would then, of course, be necessary to determine in all cases the carbonaceous residue, which might however be very large, without impairing the accuracy of the result. Still, our experience with these antimony determinations would lead us to fear that we might thus raise up as many hindrances as we avoided, and the determination we have given as No. 13 is sufficient for all purposes of comparison.

Before giving the results, it only remains to describe the manner in which the precipitates were dried, tested, and weighed. After that, by the method of reverse filtering, the precipitate had been washed, and collected in a large platinum crucible, as described on pages 14 and 15 of this article, it was dried in an air bath, at a temperature varying from 100° to 130° C. in different cases; and, with time enough, the lower temperature seemed to be equally effective. Thus in one case we have the following weights recorded: —

---

* Our experiments also indicate that, even in presence of a large excess of hydrochloric acid, the occlusion of oxichloride can be prevented by using a very large excess of tartaric acid. It was under these conditions that the determination No. 13 was made. Of course, the occlusion of tartaric acid is then large; but, as shown, this need not impair the accuracy of the result.

Weight of Sb_2S_3 dried in a steam-chest . . .	2.1700	grammes.
„ same after 30 minutes at 150° . .	2.1685	„
„ „ „ additional .	2.1685	„
„ „ conversion at 210° . .	2.1677	„

By drying, as is well known, the precipitate shrinks to a very small volume. A small portion was then taken and dissolved in hydrochloric acid, in order that we might be sure no free sulphur was present; but so effectual were the precautions against oxidation we have described, that after our process was perfected we obtained in no case the least trace of residue. The larger part of the dried precipitate was next transferred to a platinum nacelle; and, the weight of this portion having been exactly determined, the nacelle was introduced into a glass tube about three-fourths of an inch in diameter. The portion of the tube holding the nacelle was heated by an air bath, through which the tube passed and was tightly held. This air bath was made of sheet iron. It had a double bottom, and a tubulature on one side for a thermometer. The cover consisted of a thin sheet of mica, through which the nacelle could be seen within the tube, and every change accurately observed. The bath was heated by a common gas burner, and the temperature regulated by regulating the flow and pressure of the gas. During the heating, a slow current of hydrogen was passed through the tube. This gas, made from oil of vitriol, zinc, and water, in a large germinator, was first purified by passing through solutions of caustic potash and nitrate of silver, and afterwards dried by sulphuric acid and chloride of calcium. The gas entered and passed out through tightly fitting corks, and the glass exit tube was made small in order that the least condensation of moisture on its walls might be the more apparent.* In this simple apparatus, the dried precipitate was maintained at a temperature between 180° and 200°, until the weight was constant. The nacelle was then again returned to the tube and heated to 210°, or until the conversion of the red sulphide of antimony into the gray modification took place, and the weight again taken. Lastly, from the loss of weight thus observed, the correction to be subtracted from the first weight of the whole precipitate was easily calculated. It is evident that with this apparatus we were enabled to collect and examine the products sublimed during the heating, and form a very accurate estimate of the relative amounts under different conditions; and it was from the phenomena thus observed that we deduced the inferences which have already been stated. One or two additional remarks, though in part a repetition, are here important.

---

* The apparatus is the same as that subsequently used for the sublimation of bromide and iodide of antimony, and figured on page 57, with this exception, that the large adapter which there serves as a receiver is replaced by a small glass tube, as described above.

1. Although, during the course of the investigation, the experiment was repeated a great number of times, yet in no case, even when the precipitate was dried at 100°, was there the least deposition of water on the walls of the exit tube. Were there as much hygroscopic water present as has been usually supposed, it must have shown itself under these circumstances. Of course, a very minute amount would escape detection, and we sought to obtain more positive evidence, both by means of dried sulphate of copper and also by a chloride of calcium tube; but the evidence of the first was wholly negative, and from the slight and irregular variations of the last no positive indications could be drawn. In some cases, the weight of the chloride of calcium tube was obviously affected by the vapor of chloride of antimony; while in other cases, as in the example cited on page 25, the accidental variations in the weight of the tube were greater than the quantity, if any, we sought to estimate. During the charring of the occluded tartaric acid, of course some water must be formed, and the decomposition was made very evident by the familiar empyreumatic odor, which was always plainly perceptible; but the action was too complex and irregular, and the amount of the products too small, to admit of any trustworthy estimates by the usual methods.

2. The change of sulphide of antimony from the red to the gray modification is very sudden and striking. The temperature at which it takes place varies between 210° and 220°, depending on conditions which we could not wholly trace. It begins at some one point, and then spreads very rapidly through the mass. During the change, as has been stated, small particles of the material are sometimes projected from the nacelle; and there is not unfrequently evidence that at some points of the mass the temperature must have risen high enough to volatilize the sulphide of antimony. Frequently also at this time an additional amount of white sublimate was formed, and the peculiar empyreumatic odor again perceived. Under these circumstances, there was always a decided loss of weight. But at other times, especially

when the precipitate contained no oxichloride of antimony and had been heated for several hours to a temperature near the point of conversion, the change was attended with no loss of weight which was appreciable, as, for example, in the experiments cited on page 25, and in the determination numbered 13 below. After conversion, as we found in several experiments, the gray sulphide may be heated to 250° or even 300° without further loss.

The change of condition just described is not attended, however, with any very marked amount of condensation. We made the following determinations of the specific gravity of the sulphide of antimony in the two conditions. The specimens were weighed in alcohol of known density, and the specific gravity referred to water by calculation. An air pump was used to remove any entangled air.

RED SULPHIDE OF ANTIMONY DRIED AT 180°.

1. Specific Gravity determined at 26°.7 = 4.226.
2. " " " " 23°. = 4.223.

GRAY SULPHIDE OF ANTIMONY* CONVERTED AT 210°.

1. Specific Gravity determined at 28° = 4.288.
2. " " " " 27° = 4.289.

The published determinations of the specific gravity of the native antimony glance give values varying between 4.52 and 4.75; and Heinrich Rose gives † for the specific gravity of the artificial product made by melting together the constituents the value 4.614, and for the same, after pulverizing, 4.641. He also gives for the precipitated sulphide the value 4.421. It is evident, therefore, that the value varies, but in the above determinations the comparison of the two modifications were made under as nearly as possible identical conditions. Possibly, the decomposition of the occluded tartaric acid, producing a more or less spongy condition in the mass, may be the cause of the observed differences.

In the later determinations, when for the reasons we have stated the occlusion of tartaric acid was large, the gray sulphide, after having been weighed, was always dissolved in hydrochloric acid, and the carbonaceous residue estimated. The solution, having been mixed with tartaric acid and diluted with water, was filtered, and the residue collected on one of the smallest paper disks used in the process of reverse filtering. The disk was then dried and reweighed. The constancy of weight with these paper disks was very remarkable; and it may give greater confidence in the accuracy of our method to add here a few comparisons of the weights of the larger-sized disks which were used in collecting the sulphide of antimony itself, taken before and after they had been used. The first column gives the original weight of the disks, which were first dried at 120°, and then kept in an atmosphere dried by sulphuric acid. The second column gives the weight of the same after it had been used in filtering, and taken from the crucible after the first weighing with some of the dried precipitate adhering. We have only one weight of this kind recorded; but this will show how little of the precipitate adheres to the filter. The third column gives the weight of the same paper disk, after washing first with sulphide of ammonium, then with water, and drying.

---

* Same as obtained in determination of table, pages 36–7, No. 8.

† Poggendorff, Annalen, lxxxix. 122.

	I.	II.	III.
Experiment 1	0.0654 gram.	0.0686 gram.	0.0654 gram.
" 2	0.0375 "		0.0377 "
" 3	0.0457 "		0.0458 "
" 4	0.0436 "		0.0437 "

It should here be noted that in regarding all the carbonaceous residue as extraneous matter, and subtracting its weight from the total weight of the precipitate, we leave all the causes of loss in our determinations unbalanced. We estimate as sulphide of antimony the material which bears a temperature of 300° unchanged, and dissolves in hydrochloric acid; and every known cause of error must tend to diminish the weight obtained.* But less sulphide of antimony corresponds to a higher apparent atomic weight of antimony; and hence, in those determinations in which the weight of the insoluble residue has been taken into account, the tendency of all the known errors must be to increase the apparent atomic weight, and, so far as our knowledge goes, it would seem impossible that the value obtained in 13 D., for example, should be too low. Moreover, the black residue is not always wholly carbon, and at times contains some antimony compound. Any siliceous or other insoluble material which accident had introduced into the analysis would of course be eliminated as a part of the residue; and the same would be true of all forms of organic matter, as well as tartaric acid, which the precipitate might absorb from the solutions in which it formed, or from the water by which it was washed.* It may be interesting, in this connection, to add a few determinations of the relative amount of combustible and incombustible matter in a few of these residues: —

---

* Besides the causes of loss we have mentioned, and the small mechanical losses incident to every process of the kind, we must not overlook the fact that under most conditions a precipitate of sulphide of antimony is slightly soluble in the surrounding menstruum, and in our determinations this was frequently indicated by a barely visible coloration of the filtrate. Moreover, in several instances, we observed in this filtrate a condition which is familiar in titrations of silver; namely, a state in which either a solution of antimony or a solution of hydric sulphide would strike a red coloration.

No. 1.	Weight of residue	0.0067	grammes
	„ after ignition	0.0032	„
	Combustible	0.0035	„
No. 2.	Weight of residue	0.0078	„
	„ after ignition	0.0013	„
	Combustible portion	0.0065	„
No. 3.	Weight of residue	0.0064	„
	„ after ignition	0.0020	„
	Combustible portion	0.0044	„

Although this discussion of the causes of error was essential to the refinement of the process, it must not be inferred that the magnitude of these errors was proportional to the attention they have necessarily received, or that they are important except with reference to the accuracy required in the determination of an atomic weight. Except in those cases where, as has been stated, the amount was accurately determined and allowed for, the greatest possible error in either direction arising from occluded materials never exceeded a few thousandths of the weight estimated, and might safely have been neglected in an ordinary analysis. These errors, as we have stated, tend to balance each other; and their maximum effect is shown in the first two groups of determinations in the table on pages 36–7. In the group of five determinations 8–12, we endeavored, as has been stated, so to regulate the conditions that the opposite errors should balance each other; and the very remarkable agreement between these results and the mean of the first five is in itself a proof that we have been successful, and, moreover, their close agreement among themselves indicates that, so far as the mere mechanical details of the process are concerned, a perfection has been reached which will compare favorably with the most accurate methods of quantitative analysis. In order to exhibit the details of the work as far as practicable, we give below two examples of the most trustworthy determinations. The first is selected from the group 8–12, and is one in which no account is taken of the occluded material, but where it is believed that the conditions were so regulated that the two chief sources of error must on the average (not, however, necessarily in every determination) balance each other. This example is selected, because, although no account was taken of the carbonaceous residue, it was determined and examined, and thus some data are given for judging not only how large the errors were, but also how nearly they were balanced. The second example is unique. In this case, by a fortuitous concurrence of conditions, there was no oxichloride formed even in a solution containing an excess of hydrochloric acid, and no material sublimation of any antimony product. Here, then, we have fortunately a determination belonging to the same class as the others, in which the error is known to be all on one side, and where the error can be corrected by determining the carbonaceous residue. Since, moreover, in the details of its execution, this determination was faultless in every respect, the result it furnishes is of very great value as a standard of comparison. And, further, since the tendency of every known error not corrected by subtracting the carbonaceous residue is in the opposite direction, it seems impossible, at least, with our present knowledge, that the atomic weight of antimony should be greater than the value thus obtained.

---

* In one case, when no tartaric acid was used whatever, and when the antimony was kept in solution by hydrochloric acid only, as mentioned on page 22, we obtained a distinct carbonaceous residue, evidently from some organic material which the precipitate like a mordant had absorbed.

Details of Determination marked No. 11 E.

The finely pulverized antimony was weighed in a platinum nacelle. By means of a loop of platinum wire, this nacelle was lowered into a glass flask having a capacity of about 150 cubic centimetres. The powder having been shaken out, the nacelle was withdrawn, replaced on the balance pan, and weighed.

Weight of nacelle and antimony . . .	8.2655	grammes.
" " "	6.2617	"
Weight of antimony transferred to flask .	2.0038	"

The antimony was next dissolved without the aid of heat in 30 cubic centimetres of hydrochloric acid mixed with 5 cubic centimetres of decim-nitric acid. Before complete solution had taken place, the flask was connected with a reversed condenser, and the solution boiled until every trace of the metal had disappeared. Next, the antimony bullets, previously prepared as described, were added, and the boiling continued until the solution was perfectly colorless. To this solution, after cooling, was added 20 grammes of tartaric acid, dissolved in about twice its own weight of water, and the solution transferred, in the manner before described, to an Erlenmeyer flask holding about two litres.

First weight of platinum tunnel and antimony bullets,	96.8646	grammes.
Second „ „ „ „ „ „ „	96.5267	„
Weight of antimony dissolved during reduction .	0.3379	„
„ „ „ as above	2.0038	„
Total weight of antimony taken	2.3417	„

The surfaces of the bullets were not disintegrated, and there was no appearance of any antimony powder arising therefrom. After precipitation, at the ordinary temperature, the precipitate was gently digested for some time with a large excess of $H_2S + Aq$ before heating the liquid to the boiling point. Every detail was successful. The precipitate was washed six times, and collected as usual by reverse filtering in a large platinum crucible, and dried in air bath at from 120° to 130° C.

Weight of small paper disk	0.0388	grammes.
„ „ large platinum crucible . .	180.8345	„
	180.8733	„
Weight of crucible, filter, and Sb_2S_3 .	184.1580	„
Weight of red Sb_2S_3, dried at 130° . .	3.2847	„

A portion of the dried precipitate was dissolved in hydrochloric acid. It gave no residue. The rest was then transferred to a platinum nacelle, and heated, as has been described, in a current of pure and dry hydrogen gas.

Weight of platinum nacelle	6.2616	grammes.
„ „ „ „ and Sb_2S_3	9.0480	„
Weight of Sb_2S_3 transferred	2.7864	„

Weight after heating to 175° for half an hour	9.0433	grammes.
” ” ” ” ” half an hour longer	9.0433	”
Loss at this temperature	0.0047	”
Loss calculated for whole amount of Sb_2S_3	0.0055	”
Weight after heating to 210°, and converting to gray modification	9.0430	grammes.
Total loss after conversion	0.0050	”
Loss calculated for whole amount of Sb_2S_3	0.0059	”

At 175° we observed a distinct sublimate, and at 210° a slight addition to it.

Weight of red Sb_2S_3, as above	3.2847	grammes.
Loss when dried at 175°	0.0055	”
Corrected weight of red Sb_2S_3	3.2792	”
Weight of antimony taken	2.3417	”
Weight of sulphur in combination	0.9375	”

0.9375 : 2.3417 = 48 : 119.90, resulting value of Sb.

Weight of red Sb_2S_3, as before	3.2847	grammes.
Loss when dried at 210°, and converted	0.0059	”
Corrected weight of gray sulphide	3.2788	”
Weight of antimony taken	2.3417	”
Weight of sulphur in combination	0.9371	”

0.9371 : 2.3417 = 48 : 119.94, the resulting value of Sb.

During the drying and conversion of the precipitate, there was a distinct empyreumatic odor, and on dissolving the gray sulphide in hydrochloric acid a considerable amount of black residue. This residue was collected on a weighed disk of paper, and examined.

Weight of carbonaceous residue calculated for whole precipitate	0.0078	grammes.
Weight of incombustible portion	0.0013	”
” ” combustible portion	0.0065	”

Here the antimonial sublimate was but small, and the carbonaceous residue was evidently the preponderating cause of error. Hence, a result decidedly below the average. But, even if we subtract the whole of the combustible portion of this residue and leave the opposite errors uncompensated, we only raise the resulting value to 120.78.

DETAILS OF DETERMINATION MARKED 13 D.

Weight of nacelle and antimony . . .	8.2578	grammes.
” ” ”	6.2522	„
Weight of antimony transferred to flask .	2.0056	„

The metal was dissolved with 30 cubic centimetres of hydrochloric acid and 5 cubic centimetres of decim-nitric acid, as in last example. But more tartaric acid, 25 grammes, was used, and in addition 20 cubic centimetres of hydrochloric acid were added to the water in the large flask before pouring in the solution through the platinum tunnel.

First weight of platinum tunnel and antimony bullets,	95.5825	grammes.
Second „ „ „ „ „ „ „	95.2038	”
Weight of antimony dissolved during reduction . .	0.3787	
„ „ „ as above	2.0056	”
Total weight of antimony taken	2.3843	”

Here the same remarks apply as were made at the corresponding stage of the previous example.

Weight of small paper disk	0.0436	grammes.
” „ large platinum crucible . .	180.8315	”
	180.8751	”
Weight of crucible, filter, and Sb_2S_3 .	184.2290	”
Weight of Sb_2S_3, dried at 130°	3.3539	”

Most of the precipitate was transferred to a platinum nacelle, and heated as before described.

Weight of platinum nacelle	6.2518	grammes.
” ” ” ” and Sb_2S_8 .	9.4242	”
Weight of Sb_2S_3 transferred	3.1724	”

Weight after heating for some time at from 175° to 195°	9.4200	grammes.
Weight after conversion 210°	9.4200	„
Loss at either temperature	0.0042	„
Loss calculated for whole amount of Sb_2S_3	0.0044	„

Only a very faint sublimate was formed, but we noticed a very marked empyreumatic odor. We therefore infer that the loss of weight was caused wholly by the decomposition of the occluded tartaric acid, and on dissolving the gray sulphide in hydrochloric acid we obtained a large amount of carbonaceous residue, which was collected on a paper disk, and weighed.

Weight of paper disk, dried	0.0280	grammes.
„ „ „ „ and residue	0.0400	„
„ „ residue	0.0120	„
Weight of residue calculated for whole amount of Sb_2S_3	0.0126	„

Hence we have —

Weight of Sb_2S_3 dried at 130°, as before		3.3539	grammes.
Loss on heating to 210°	0.0044		
Carbonaceous residue	0.0126	0.0170	„
Estimated as pure Sb_2S_3		3.3369	„
Weight of antimony taken		2.3843	„
Weight of sulphur in combination		0.9526	„

0 : 9526 : 2.3843 = 48 : 120.14, the resulting value of Sb, whether we take the red or the gray sulphide.

The above examples will illustrate how the results were obtained which are tabulated on pages 36–7.

SYNTHESIS OF

No.		Wt. in gram of Sb taken.	Wt. dissolved from balls.	Total weight of Sb used.	Wt. of red Sb_2S_3 dried at 180° C.
1.	A.	2.0036	0.2023	2.2059	3.0898
2.	E.	2.0017	0.2662	2.2679	3.1778
3.	E.	2.0113	0.0853	2.0966	2.9383
4.	A.	1.9973	0.0798	2.0771	2.9051
5.	E.	2.0019	0.1087	2.1106	2.9508
		Mean of 5 Determinations		. . . .	. . . .
6.	A.	1.7638	0.0430	1.8068	2.5301
7.	A.	2.0275	0.0894	2.1169	2.9639
8.	B.	2.0116	0.0188	2.0304	2.8423
9.	B.	2.0027	0.1000	2.1027	2.9429
10.	E.	2.0015	0.1424	2.1439	3.0025
11.	E.	2.0038	0.3379	2.3417	3.2792
12.	E.	2.0014	0.2168	2.2182	3.1061
		Mean of last 5 Determinations		. . . .	. . . .
13.	D.	2.0056	0.3787	2.3843	3.3369
		Mean of the 13 Determinations		. . . .	. . . .

---

* Large residue of carbon, small sublimate.
† Small residue of carbon, large sublimate.
‡ Weight of black sulphide not found.
§ Both residue and sublimate small.

SULPHIDE OF ANTIMONY.

Per cent of S in same.	Corresponding At. Wt. of Sb when S = 32.	Wt. of black Sb_2S_3 dried at 210° C.	Per cent of S in same.	Corresponding At. Wt. of Sb when S = 32.
28.61	119.79	3.0881	28.57	120.02*
28.63	119.64	3.1764	28.60	119.82*
28.65	119.56	2.9350	28.57	120.03*
28.50	120.41	2.9021	28.43	120.85†
28.47	120.57	2.9486	28.42	120.89†
28.572	119.994	. . . .	28.518	120.322
28.59	119.91	. . . .	. . . .	. . . .‡
28.57	119.97	. . . .	. . . .	. . . .‡
28.57	120.04	2.8410	28.53	120.23§
28.55	120.13	2.9409	28.50	120.41§
28.58	119.94	2.9981	28.49	120.47§
28.59	119.90	3.2788	38.58	119.95§
28.59	119.92	3.1022	28.50	120.44§
28.576	119.986	. . . .	28.520	120.298
28.55	120.14	3.3369	28.51	120.14‖
28.5731	119.994	. . . .	28.522	120.295

‖ No sublimate or loss of weight on drying and conversion. Residue large, but weighed and subtracted. The best determination, and as perfect as can be made under conditions.

This point in our investigation was reached in the spring of 1876, and the results given above were presented to the American Academy of Arts and Sciences at their meeting of June 14th, 1876.* But although they agreed so closely with the results of Schneider, and although the close confirmation of his analysis thus furnished by our synthesis seemed so conclusive, yet we could not rest satisfied so long as the great discrepancy between this value of the atomic weight and the higher number obtained by Dumas remained unexplained. We therefore determined to repeat his experiments before publishing our results. Accordingly, in the autumn of 1876, we purified and analyzed a large number of different specimens of antimonious chloride, and the results are united in the following table. Beginning with crystallized chloride of antimony obtained from different dealers, and pure in a commercial sense, we first boiled for several hours the melted chloride over finely pulverized metallic antimony, using for the purpose a glass retort, so tilted that the condensed liquid flowed back into the body of the vessel. When boiled in this way, the surface of the vapor is marked by a very well-defined ring in the neck of the retort; and by regulating the lamp this ring can readily be maintained very near the mouth, so that, while all the chloride of antimony condenses and flows back, any more volatile admixtures will gradually escape. The retort having been brought into its normal position, the chloride of antimony was next distilled; and, rejecting the first and last eighth which came over, the rest of the product was redistilled over strips of metallic zinc, and so on three or four times, rejecting at each distillation the first and last of the product. The final distillate was then still further purified by repeated crystallizations from fusion. As the fused mass solidifies quite slowly (indicating a large loss of latent heat), it is easy to arrest the process at any point, and pour off the still liquid portion from the crystals which have formed. The last can then be remelted, and the process repeated, and so on indefinitely as long as the material lasts. In this way, from several kilogrammes of the commercial chloride we obtained the few grammes of beautifully clear and perfect crystals used in our analyses. In the fifth preparation, the crystals were obtained not by fusion, but by cooling a saturated solution of the previously distilled chloride in purified sulphide of carbon. Such a solution, saturated at the boiling point of sulphide of carbon, deposits the larger part of the chloride, when cooled to the ordinary temperature. Naturally, every precaution was taken during the course of these preparations to protect this exceedingly hygroscopic substance from contact with moist air, and all the transfers were made in a portable photographic developing chamber, the air of which was kept dry by dishes of sulphuric acid. The portions for analysis were transferred, in this chamber, to tightly fitting weighing tubes; and, after the weight was taken, they were dissolved in a concentrated aqueous solution of tartaric acid, using about 5 grammes of tartaric acid to each gramme of chloride of antimony. The solutions were then diluted, and precipitated with argentic nitrate, weighing out in each case the amount required, so that only the least possible excess of the reagent should be added. The precipitates were washed and collected by reverse filtering in platinum or porcelain crucibles, and dried in an air bath at temperatures varying from 110° to 120°. They were weighed with the small disk of paper used in this process, and the invariability of the weight of these paper disks was repeatedly tested. Also, in several instances after removing the filter, the argentic chloride was heated to incipient melting; but, as in no case was its weight thus altered, this additional precaution seemed unnecessary. In the determination numbered 17, an attempt was made to ascertain whether the presence of antimony in the tartaric acid solution appreciably influences the precipitation of argentic chloride. In this analysis, the antimony was first separated from the solution by H_2S; and, the excess of this reagent having been removed by warming the filtrate with a small amount of ferric nitrate, the chlorine was precipitated in the usual way. The result, as will be seen, agrees as nearly as could be expected with those obtained by at once precipitating the chlorine from the antimony solution; and it was not until some time subsequently that the causes of error referred to on page 5 were discovered.

---

* These Proceedings, vol. xii. p. 282.

The letters in the following table indicate different preparations, thus:—

a was made from a crystallized chloride of Veron and Fontaine, Paris, which was purified in the manner described above.

b was made from a crystallized chloride marked Rousseau Frères, Paris, purified as before.

c was the same as *b*, again distilled and crystallized.

d, the same as *c*, after ten additional distillations.

e, the same as *d*, again distilled below 100° in a current of dry hydrogen gas.

f was made with a crystallized chloride from Merck of Darmstadt, purified by repeated distillations and subsequent crystallizations from bisulphide of carbon, after first treating with chlorine as described beyond.

g, same as *f*, but in this determination the antimony was first precipitated from the solution.

ANALYSIS OF ANTIMONIOUS CHLORIDE.

DETERMINATION OF CHLORINE.

No.	$SbCl_3$. grammes.		AgCl. grammes.	% of Chlorine. Cl = 35.5. Ag = 108.	At. Wt. of Sb. Cl = 35.5
1 *a.*	1.5974	yielded	3.0124	46.653	121.78
2 *a.*	1.2533	„	2.3620	46.623	121.93
3 *a.*	0.8876	„	1.6754	46.696	121.57
4 *b.*	0.8336	„	1.5674	46.516	122.46
5 *b.*	0.5326	„	1.0021	46.546	122.30
6 *b.*	0.7270	„	1.3691	46.588	122.10
7 *c.*	1.2679	„	2.3883	46.599	122.04
8 *c.*	1.9422	„	3.6646	46.678	121.66
9 *c.*	1.7702	„	3.3384	46.655	121.77
10 *d.*	2.5030	„	4.7184	46.635	121.87
11 *d.*	2.1450	„	4.0410	46.616	121.96
12 *e.*	1.7697	„	3.3281	46.524	122.42
13 *e.*	2.3435	„	4.4157	46.613	121.98
14 *f.*	1.3686	„	2.5813	46.659	121.75
15 *f.*	1.8638	„	3.5146	46.650	121.79
16 *f.*	2.0300	„	3.8282	46.653	121.78
17 *g.*	2.4450	„	4.6086	46.630	121.89
	Mean value for all analyses			46.620	121.94
	Theory when		Sb = 122	46.608	122.
	„	„	Sb = 120	47.020	120.

If in calculating the per cent of chlorine from the results of the above determinations we use the atomic weights for silver and chlorine obtained by Stas (namely, $Cl = 35.457$ and $Ag = 107.93$), these per cents will be in each case very nearly 0.020 lower, and we shall obtain for the mean value 46.600 instead of 46.620. Moreover, on this assumption the atomic weight of antimony, deduced from Dumas's analysis of the chloride, would be 121.95 instead of 122. Again, if we use Stas's value of the atomic weight of sulphur ($S = 32.074$) in calculating the atomic weight of antimony from our own results, on the synthesis of the sulphide, we should obtain 120.28 instead of 120; and, lastly, the values $Sb = 120.28$ and $Cl = 35.457$ give for the per cent of chlorine in antimonious chloride the value 46.931.

Here, then, is a most striking result; for these determinations confirm the value of the atomic weight of antimony obtained by Dumas as closely as did the previous determinations confirm that obtained by Schneider. Evidently, there was a large constant error in one case or the other. Moreover, it appeared improbable that in either case any error could arise in the chemical process employed: for, in the first instance, we had a synthesis by one method confirming an analysis by a wholly different method; and, in the second instance, the analytical process employed is regarded as one of the most accurate known to science, and we had apparently shown that its accuracy was not impaired under the peculiar conditions present. It appeared, therefore, reasonable to assume that the results did truly indicate both the actual proportion of antimony in the sulphide of antimony and of chlorine in the chloride of antimony analyzed, and to look for the cause of the discrepancy to some impurity in one or the other compound. We therefore next sought to determine how much sulphide of antimony could be obtained from a given weight of chloride of antimony, hoping that by thus bringing the relations of antimony to chlorine and sulphur into close comparison the source of the error might be indicated.

The precipitation of sulphide of antimony from a solution of the chloride in tartaric acid is made under conditions which are far more favorable to accurate results than those with which we were obliged to contend in our previous experiments. If the solution is diluted with water charged with carbonic dioxide, and if the precipitation is made in the way we have described,* we can avoid all excess of hydrochloric acid except that which is formed by the chemical reaction, and there is then no oxichloride of antimony formed, and no subsequent loss of chloride of antimony on heating the red sulphide up to the point of its conversion to the gray modification. Moreover, less tartaric acid is required, — not more than 6 grammes to every gramme of chloride, — and consequently less is occluded by the precipitate, so that with care the carbonaceous residue can be reduced to an insignificant amount.

---

* See page 14.

The following table exhibits the results of these antimony determinations, as well as the general result of the assumed complete analysis of antimonious chloride. The per cent of chlorine taken is the mean of the first thirteen determinations of the previous table, as these only had been made at the time the second table was drawn up, and it therefore exhibits the results exactly as they were presented to us at this stage of the investigation.

ANALYSIS OF ANTIMONIOUS CHLORIDE.

DETERMINATION OF ANTIMONY.

	$SbCl_3$ taken in grammes.	Sb_2S_3 obtained in grammes.	% of Antimony when Sb : S = 120 : 32.*	% of Antimony if Sb : S = 122 : 32.†
1 *b.*	3.8846	2.8973	53.275	53.525
2 *b.*	5.1317	3.8417	53.473	53.725
3 *b.*	4.4480	3.3201	53.316	53.567
4 *b.*	4.5506	3.4009	53.882	53.633
5 *b.*	4.8077	3.6072	53.593	53.845
6 *b.*	4.2774	3.1958	53.367	53.618
Mean of all Analyses			53.401	53.652

MEAN RESULT OF COMPLETE ANALYSIS.

Antimony, the mean of six determinations	53.401	53.652
Chlorine, „ „ thirteen „	46.611 ‡	46.611 ‡
	100.012	100.263

---

* Or assuming that $\frac{5}{7}$ of the gray sulphide is antimony, as deduced from actual synthesis.

† According to the generally accepted theory.

‡ When Cl = 35.5 and Ag = 108, according to Dumas.

As they at first presented themselves to us, these new results, so far from throwing light on the subject, only rendered the problem the more obscure and baffling. Towards interpreting them however, one point seemed evident; — that, however little value our own experiments and those of Schneider might have in fixing the atomic weight of antimony, they had at least established, beyond all doubt, the proportion of this element in the gray sulphide weighed in our antimony determinations. For if we assumed, as those experiments indicated, that five-sevenths of the gray sulphide was antimony, then the amounts of antimony and chlorine found in the analysis of antimonious chloride just made almost exactly supplemented each other; while on the other hand, if this material was, as generally believed, pure Sb_2S_3, in which $Sb : S = 122 : 32$, then our determinations of one or the other of these elements must be greatly erroneous, and the excess obtained far too great to be explained by any known or probable imperfections of our methods. Of course, although the gray sulphide might contain, on the average, five-sevenths of its weight of antimony, it was a possible supposition that it might also occlude a constant amount of some undiscovered impurity, leaving the proportion of the sulphur to the antimony that which the atomic weights 122 and 32 required; and, were it not for our previous experience, this would have been the most obvious explanation of the discrepancy. Indeed, the new facts led us to re-examine this material, and review our previous conclusions, but with the same result as before. We could discover no impurity except the small amount of carbonaceous material which was so well known and taken into the account, and in our later determination (as is shown by the example on page 69) even this had been reduced to so small an amount as to be wholly insignificant. It is very difficult in any such case to prove a negative, but in the present instance the following considerations appeared conclusive, which on account of their important bearing we in great part recapitulate, although the evidence was again reviewed at this time.

1. Such an impurity must be comparatively large in quantity, not less than several centigrammes in the amount of the gray sulphide usually weighed.

2. It must exist to an equal extent in both the native sulphide and the artificial product of our analytical process, for both contain the same percentage of antimony.

3. It must be derived from antimonious chloride, tartaric acid, hydric sulphide, and water, which were the only reagents used in the process, and from these in the purest condition they could be obtained.

4. It must be able to bear a temperature of 300°C. without alteration, for in our later determinations the sulphide was heated to this temperature.

5. It must be soluble in hydrochloric acid; for allowance was made for the impurity which remained undissolved when the sulphide was decomposed by this reagent.

Hence, it still appeared, as before, quite impossible that any such impurity could be present; but, in order to eliminate even more certainly any unforeseen and accidental conditions, we made the following experiments.

In the first place, we brought together the aqueous solutions of hydrochloric acid, tartaric acid, and sulphide of hydrogen in the same proportions, and under the same conditions in which they were used in our antimony determinations; but, although we made several trials, we obtained in no case the slightest precipitate.

In the second place, we heated a small amount of the tartaric acid used to 300° C., treating it exactly in the same way as the precipitated antimonious sulphide in our analytical processes; and we found that the small amount of carbonaceous residue obtained was wholly insoluble in hydrochloric acid.

It would evidently have been more satisfactory to be able to determine the amount of combined sulphur in the gray sulphide, and thus to prove that it exactly supplemented the antimony, as we had endeavored to do in the case of the antimonious chloride; but unfortunately we could devise no method which promised to be satisfactory. We were obliged therefore to rest on the negative evidence, and this seemed to exclude the most obvious explanation of our contradictory results. Of course, we could not reasonably entertain the question that the large excess which the analyses of table pages 40 and 42 presented, when calculated for $Sb = 122$, was due wholly to an overestimate of the chlorine, because the amount of chlorine was only that which this theory of the composition of $SbCl_3$ required; and, moreover, the constancy in the composition of the chloride, after it had been submitted to such various treatment, was surprisingly great, and served to exclude the idea of any error at all comparable with that which the excess in question would imply. We had found apparently that the composition remained sensibly constant, even after the successive distillation of what we had regarded as essentially pure material. We had distilled it in a current of perfectly dry hydrogen, at a temperature below 100°, and still obtained in the distillate the same composition as before. We now further made the four additional chlorine determinations, Nos. 14 to 17, in the table on page 40. The material for these analyses was first purified by repeated distillations as before, first over powdered antimony and then over zinc. Through the melted chloride was then passed, for a short time, a current of dry chlorine gas, in order to make sure that no such thing as a subchloride of antimony, if it can exist, or particles of metallic antimony, could be present. The chloride was then again redistilled several times, and this product purified by ten or twelve repeated crystallizations from a solution in disulphide of carbon, the material being protected all the time as far as possible from contact with moist air. The few grammes of pure chloride thus obtained from more than a kilogramme of so-called pure commercial chloride of antimony were submitted to analysis, and, as will be noticed, the results were in complete accordance with those we had obtained before. Lastly, we found nearly the same result, with only the little loss that was to be expected, when the antimony was removed from the solution before precipitating the chlorine.

Now, it is evident that, if the sulphide of antimony we weighed is pure, we are forced, even by these last analyses, to the conclusion that the atomic weight of antimony must be very nearly at least 120, if that of sulphur is 32, although the singular discrepancy which our results presented served at the time to render the problem exceedingly puzzling. The facts indeed seemed to indicate that, while antimony combined with chlorine in the proportion of 122 to 3 times 35.5, it combined with sulphur in the proportion of 120 to $\frac{3}{2}$ times 32, or 122 to $\frac{3}{2}$ times 32.53; in other words, that the relation of the atomic weights of chlorine and sulphur was not as accepted 35.5 to 32, but 35.5 to 32.53. And, although, after the investigations of Dumas, Stas, Marignac, and others, it was clearly out of the question that these values should be in error to the extent indicated, yet, as we have seen, Stas had found for the atomic weight of sulphur 32.074, and the results of our synthesis of sulphide of antimony calculated on this basis would give for the atomic weight of antimony 120.28. Moreover, it appeared that when the analyses of antimonious chloride made by Dumas were recalculated with Stas's values of the atomic weights of chlorine and silver ($Cl = 35.457$, $Ag = 107.93$), they gave for the same atomic weight the number 121.95. This reduced the difference between the two determinations to 1.67, and it did not seem impossible that the whole discrepancy might result from the accumulation of a number of similar small errors. We were thus led to undertake a new comparison of the atomic weights of chlorine and sulphur, based on the precipitation of sulphide of silver, by the same process we had employed in precipitating sulphide of antimony, not with any expectation of correcting the atomic weight of sulphur, but with a view possibly of verifying the higher value obtained by Stas, and more especially of still further testing the accuracy of our method of precipitating sulphides; as it was obvious that any hidden sources of error which could have impaired the accuracy of our antimony determinations might be expected to reappear in the experiments with silver, and then the well-established composition of sulphide of silver would help us to detect them.

We began these experiments by taking two adjacent portions of the same piece of pure silver foil, and, having dissolved each in nitric acid, we in the first place precipitated the silver from both solutions, as chloride, with the usual precautions. The argentic chloride from the first solution was washed, collected, and weighed as before described. That from the second solution, having been thoroughly washed by the process of reverse filtering, was redissolved in the same vessel with pure aqua-ammonia, and from this solution the silver was precipitated as sulphide by adding the supersaturated solution of hydric sulphide, using the same precautions with which we were familiar in the precipitation of sulphide of antimony. The sulphide became granular on boiling, and was readily washed and collected by the method of reverse filtering. We thus hoped to obtain a direct comparison of the atomic weights of chlorine and sulphur, not depending on the absolute purity of the metallic silver used, and moreover to obtain a confirmation or otherwise of the general accuracy of our method of determining sulphide of antimony; for it was obvious that the same causes of error were likely to inhere in two such similar processes. Hence, although such experiment would probably only confirm values already well established, such a confirmation would give us confidence in the accuracy of our previous work. But although the mechanical details of the process appeared perfect, and the results were not inconsistent with the accepted values of the weights under discussion, yet they were neither sufficiently sharp nor constant to answer the questions we had proposed, owing probably to some slight solvent action of the ammoniacal menstruum on the precipitated sulphide of silver. We were therefore led to modify the process by first preparing pure sulphide of silver by the method we have described, and then determining the relation of silver to sulphur by reducing weighed portions of this sulphide in a stream of hydrogen gas. This result, compared with the already well-known relation of silver to chlorine, — probably the most accurately determined of all the atomic ratios, — would give us the relation of sulphur to chlorine which we sought, and under essentially the same conditions as before. As thus modified, the method gave exceedingly sharp results, and the whole course of the analytical process seemed favorable to extreme accuracy. The reduction of the sulphide takes place at a temperature far below the melting point of silver, — indeed, below a visible red-heat, — and the metal separates in a most beautiful fine filamentary condition, which very greatly facilitates the reducing action of the hydrogen gas. Here again, however, we encountered another of those unforeseen constant errors which have caused us so much perplexity and fruitless labor during the whole investigation; and we give in the following table a series of results which have no other value than as illustrating the remark we have before made, that no amount of accordance in the results of the same analytical process is a sufficient guarantee against errors of this class: —

REDUCTION OF ARGENTIC SULPHIDE.

FIRST SERIES OF EXPERIMENTS AT FULL RED HEAT.

No.	Weight of Ag_2S, taken in grammes.	Weight of S, or loss during reduction.	Corresponding At. Wt. of S when Ag = 108.
1, *a.*	1.3380	0.1749	32.48
2, *b.*	1.2089	0.1582	32.52
3, *c.*	2.6592	0.3476	32.48
4, *c.*	1.9419	0.2540	32.50
5, *d.*	3.2784	0.4283	32.47
6, *e.*	2.4036	0.3143	32.49
7, *f.*	2.8359	0.3711	32.52 *

Mean value 32.494
Extreme variation from mean 026

The sulphide used in the first five determinations was prepared from washed chloride of silver, which was dissolved in pure aqua-ammonia and precipitated with $H_2S + Aq.$, as described above. The portions used in the last two determinations marked *e* and *f* were precipitated from ammonio-argentic nitrate, prepared in the first case from metallic silver, and in the last case from crystallized nitrate of silver, with the least possible excess of ammonia. During the process, a current of CO_2 was passed through the solution, which was boiled with the precipitate until all odor of ammonia had disappeared, when violent bumping ensued. After having been collected and dried, the sulphide was heated, in the first case to 280°, and in the last case to 300°, in a current of CO_2. We observed no sublimate, and there was no loss of weight with either preparation. Of the preparation *d*, seven grammes were boiled with strong hydrochloric acid until completely converted into chloride, which was then tested for sulphur, but none could be detected. The products of the decomposition of several of the preparations were tested for ammonia, and other volatile bases which might possibly have been occluded by the precipitated sulphide. Ammonia was at first found in abundance, but this was soon traced to an impurity in the hydrogen used in the reduction; and after this source of error was removed not the smallest quantity of any such product could be detected. It will thus be seen that these very closely according results were obtained with seven different preparations, made in part by different processes; and, further, that we had the strongest evidence of the purity of the material used; and, lastly, that the perfect metathesis of the sulphide with hydrochloric acid, leaving no residue of either elementary substances, proved that the silver was united to the sulphur in atomic proportions. Nevertheless, all these determinations were in error, and the error arose in this way: —

---

* In this determination, the reduced silver fused.

The argentic sulphide, held by a porcelain nacelle in a porcelain tube heated by a gas furnace, was reduced in a current of hydrogen gas. The hydrogen was prepared in an automatic generator, from clippings of sheet zinc, common sulphuric acid, and water, in the usual way; but, before reaching the porcelain tube, passed through a very long series of purifiers and driers, containing in order quick lime, soda lye, solution of acetate of lead, solution of argentic nitrate, sulphuric acid, and chloride of calcium. The object we had chiefly in view was to remove from the gas any traces of arseniuretted hydrogen or similar compounds; and we felt assured of its purity in this respect, on finding that it formed no metallic mirror even after passing for several hours through a glass tube heated to redness, and caused no darkening of "lead paper" after very prolonged exposure. The reduction of the sulphide of silver was of course attended with the evolution of hydric sulphide, and the process was continued until no trace of this substance could be detected with "lead paper" in the gas which escaped from the porcelain tube. It was evident from the first that, as already stated, the reduction could be at least nearly completed below visible redness; and, as we now know, argentic sulphide can be perfectly reduced at this low temperature, but in all the earlier determinations we found it necessary to raise the temperature at the end of the process to a full red heat, and continue the heating for several hours before the untarnished lead paper indicated that the evolution of hydric sulphide had ceased. We subsequently discovered that this effect was due to the presence of the finely divided silver, determining a reducing action of the hydrogen on certain impurities which the gas had contracted from the crude sulphuric acid, and which had escaped all the purifiers. These impurities contained both nitrogen and sulphur, and, when reduced by hydrogen in presence of the metallic silver, yielded both ammonia — to which we have already referred — and also the hydric sulphide which had misled us in regard to the completion of the reduction. On passing the gas through a glass tube containing platinum sponge, heated to low redness, the effect was still more marked; and, on placing this tube after the first alkaline purifier, the products just named were evolved in abundance, although previously, even at this point, the gas produced no effect on "lead paper." We thus traced the impurity back to the hydrogen generator, and were able to remove it by placing in the line of the purifiers a glass tube filled with platinum sponge, and heated by a combustion furnace. The tube was placed, as above described, after the alkaline purifier; and from this the gas was passed through several purifiers containing a solution of nitrate of silver, and through driers containing in part sodic hydrate and in part calcic chloride. Afterwards, the nitrate of silver in the purifiers was replaced by alkaline and acid solutions of potassic permanganate, as recommended by Schobig,* which were, at least, equally efficient. The crude acid used in the generator was found to contain an unusual amount of nitric acid, and the impurity contracted by the hydrogen was probably some volatile compound of oxygen nitrogen and sulphur, similar to that with which we are so familiar in the sulphuric acid chambers. Misled, as we have seen, by the indications of sulphur, we continued the reduction — in the experiments whose results have been given on page 47, — far longer and at a far higher temperature than was necessary; and the apparent increased value of the atomic weight obtained was due to a slight volatilization of the metallic silver. Except in one of the experiments, the temperature had never reached the melting point of silver; but, as soon as our suspicions were aroused, we detected a slight mirror near the open end of the reduction tube, which, when dissolved off with a few drops of nitric acid, and tested with hydrochloric acid, gave abundant evidence of what had taken place. And, by subsequent experiments in a stream of hydrogen gas, we found that, under the conditions present in our experiments, silver volatilized — very slightly, it is true, but markedly — at a temperature considerably below its melting point.

---

* Jour. pr. Ch. (2), xiv. 289, Oct., 1876.

We have thus shown, first, that recently reduced silver exerts a catalytic action precisely similar to that of spongy platinum, although not so powerful; and, secondly, that under these conditions the silver slowly volatilizes, at a temperature considerably below its melting point. Whether the volatilization is increased by the catalytic action, or why, in our experiments, the loss should have been so constant in amount, we have had no opportunity to determine. It was only necessary at the time to establish the fact that the results were vitiated by this constant error, and we at once hastened to determine whether the sulphide could be perfectly reduced at a temperature below that at which silver volatilizes in a current of pure hydrogen. To this end, we made many experiments, carefully testing in each case the reduced silver for sulphur, and examining with the greatest care the interior surface of the porcelain tube for any evidence of volatilization. We thus found that, by regulating the temperature, sulphide of silver could be perfectly reduced at a low red heat, without giving any evidence of loss from this cause. The following determinations were made in this way:—

REDUCTION OF ARGENTIC SULPHIDE.

SECOND SERIES OF EXPERIMENTS AT LOW RED HEAT.

No.	Wt. of Ag_2S, grammes.	Wt. of S by loss.	At. Wt. of S. Ag = 108.	At. Wt. of S. Ag = 107.93.
1, *a*.	7.5411	0.9773	32.160	32.139
2, *a*.	5.0364	0.6524	32.143	32.122
3, *b*.	2.5815	0.3345	32.155	32.134
4, *c*.	2.6130	0.3387	32.168	32.147
5, *d*.	2.5724	0.3334	32.164	32.143
Mean value			32.158	32.137
Extreme variation from mean .			0.015	0.015

In this series, as in the last, the letters indicate different preparations. The two marked *a* and *b* were both made from washed chloride of silver, dissolved in pure aqua-ammonia; that marked *c* was made from pure nitrate of silver, first converted into ammonio-nitrate, with the least possible excess of ammonia; that marked *d* was precipitated directly from a dilute aqueous solution of the same argentic nitrate, without ammonia, and was therefore formed in an acid solution. They were all precipitated with a supersaturated solution of hydric sulphide, and during the precipitation and subsequent boiling a current of carbonic dioxide was passed through the liquid. After the material had been placed in the nacelle for reduction, it was heated to 300°, in a current of carbonic dioxide, before the weight was taken. These facts are stated, because, as will be seen, the close accordance of the results obtained furnishes the strongest evidence of the uniform purity of the material prepared in the several ways we have described, and gave us great confidence in the perfection of our new method of precipitating sulphides.

Stas obtained for the atomic weight of sulphur when $Ag = 107.93$ the value 32.074, and the mean of our results differs from his by only 0.063. How small this difference really is, is shown by the fact that even with the largest quantity of sulphide used, — which required a platinum nacelle 5 inches long by $1\frac{1}{8}$ inches wide to hold the spongiform* mass of reduced silver, — the difference in question only corresponds to $1\frac{7}{10}$ milligrammes in the weight estimated; and with the smaller quantities — which required the largest porcelain nacelle we could obtain — the difference only corresponds to about half a milligramme. Still, the process is sufficiently accurate to show even this difference; for the extreme variations from the mean value in the last series of results only corresponds for the larger quantities to $\frac{4}{10}$ of a milligramme, and for the smaller to $\frac{15}{100}$ of a milligramme of the quantity estimated. The difference, therefore, small as it is, evidently points to a constant error of some kind, which, as we suspect, is caused by a slight volatilization of silver, even at this comparatively low temperature, although we were unable to obtain any other evidence of it. Hence, the following two additional determinations may be of interest, in which the sulphide was reduced below a visible red heat, in a small platinum nacelle, heated in a tube of hard glass: —

---

* The production of moss silver in this process is a most beautiful phenomenon, which has been described by Dr. Percy, "Metallurgy," I. 360, and more recently by Professor Liversidge, of the University of Sydney.

REDUCTION OF ARGENTIC SULPHIDE.

THIRD SERIES OF EXPERIMENTS, TEMP. BELOW VISIBLE REDNESS.

No.	Wt. of Ag_2S. grammes.	Wt. of S. by loss.	At. Wt. of S. Ag = 108.	At. Wt. of S. Ag = 107.93.
1.	1.1357	0.1465	31.990	31.969
2.	1.2936	0.1670	32.010	31.990
Mean value			32.000	31.980

We are sure that in these experiments no silver was lost, because the least trace of sublimate would have been visible on the glass. We cannot be so certain that a trace of sulphide did not remain unreduced; but we do feel confident that the true value of the atomic weight of sulphur — so far, at least, as it can be determined by the analysis of argentic sulphide — must lie between the limits which the two last series of experiments fix. This is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end.

While, therefore, this portion of our investigation was not wanting in interesting results, it did not help us to explain the discrepancy we had observed in our experiments on the atomic weight of antimony. We now felt, however, greater confidence in our synthesis of sulphide of antimony; for if the sulphide of silver we had analyzed was so pure there was every reason to believe that the sulphide of antimony prepared in the same way was equally pure, save only the small occlusions which were so well known, and had been taken into account. We were therefore now still more fully persuaded that the value 120, which we had obtained for the atomic weight of antimony, must be correct within a few tenths of a unit; and it seemed to us very clear that the constant error, which had so perplexed us, was to be looked for in the analyses of chloride of antimony. Moreover, it seemed probable to us at this time that we might obtain a clew to the hidden source of error by analyzing the bromide and iodide of antimony before continuing our experiments on the chloride, for the same influences would be likely to affect all these processes; yet it was reasonable to expect that they would act in varying degrees in the three cases, and that they might thus reveal their nature. We begin with our work on the bromide.

We prepared the bromide of antimony by adding in small portions at a time the pulverized metal to a strong solution of bromine in sulphide of carbon. The retort containing the solution was kept cool by snow, and shaken after each addition until the action ceased. As soon as the color of bromine was discharged, the sulphide of carbon was distilled off over a water bath; and then, replacing the water bath with a gas lamp, the bromide of antimony was first boiled, and then distilled over the finely powdered antimony which had been added in excess. On account of the high boiling point of bromide of antimony, and the readiness with which its vapor condenses, it was found best in distilling to cover the body of the retort with a hood. The bromide thus prepared was purified by repeated distillations over pulverized antimony, as in the case of the chloride, and finally by crystallizing and recrystallizing several times from solution in purified sulphide of carbon. A warm saturated solution in sulphide of carbon deposits, when cooled to the freezing point, the greater part of the bromide of antimony in fine acicular crystals. These crystals were dried first with blotting-paper, and then *in vacuo* over sulphuric acid. The antimonious bromide thus purified by fractional distillation and crystallization was only a very small fraction of the first crude product. It was pure white, had a high silky lustre, and, when first made, was wholly destitute of odor. It was carefully examined for chlorine, iodine, and arsenic; but the delicate test which we possess for all three of these elements, so frequently associated with commercial antimony and bromine, failed to show the least trace of either in the bromide of antimony we analyzed. The determinations of bromine were made in all respects like those of chlorine. Great care was taken not to add more than a very slight excess of argentic nitrate, and we found that under these conditions the supernatant liquid cleared more readily above the precipitate in the case of bromide of silver than with the corresponding chloride, and for this reason the first could be washed more quickly than the last. The results of these determinations are embodied in the table on the following page.

Here, as before, the letters indicate different preparations: *a* was made and purified as described above; *b* was the same material as *a* redistilled and again crystallized from bisulphide of carbon; *c* was another portion of the same material several times redistilled and twice recrystallized from the same solvent; *d* was a separate preparation from the start; *e* was another separate preparation purified with extreme care. In the last case there was over a kilogramme of the crude product, which was reduced by the fractional distillation and crystallization — each process repeated from ten to twenty times — to the few grammes used in the analyses. These methods of purifying the substance were thus pushed to their utmost limits.

ANALYSES OF ANTIMONIOUS BROMIDE.

DETERMINATION OF BROMINE.

No.	Wt. of Sb Br_3 taken in grammes.	Wt. of Ag Br obtained.	% of Bromine. Br = 80, Ag 108.
1, *a.*	1.8621	2.9216	66.765
2, *a.*	0.9856	1.5422	66.584
3, *b.*	1.8650	2.9268	66.779
4, *b.*	1.5330	2.4030	66.703
5, *b.*	1.3689	2.1445	66.663
6, *c.*	1.2124	1.8991	66.655
7, *c.*	0.9417	1.4749	66.647
8, *d.*	2.5404	3.9755	66.593
9, *d.*	1.5269	2.3905	66.623
10, *e.*	1.8604	2.9180	66.743
11, *e.*	1.7298	2.7083	66.624
12, *e.*	3.2838	5.1398	66.604
13, *e.*	2.3589	3.6959	66.671
14, *e.*	1.3323	2.0863	66.635
15, *e.*	2.6974	4.2285	66.708

Mean value from last six determinations . 66.664

Mean value from all the determinations . 66.6665

Theory Sb 120 requires 66.6666

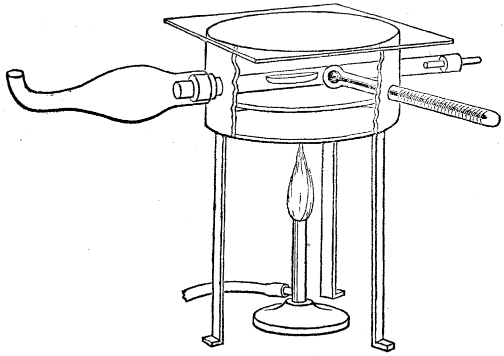
Theory Sb 122 „ 66.2983

If in calculating the results of the above bromine determinations we use the atomic weights of Stas, — Br = 79.952, Ag = 107.93, — the per cents found will be in each case only 0.002 higher, which is, of course, an inappreciable difference. Hence, whether we take Stas's or Dumas's values for the atomic weights of bromine and silver, the atomic weight of antimony deduced from the above determinations is exactly 120.00.

This is certainly a remarkably close confirmation of our previous conclusion. Indeed the wonderful coincidence between the observed and the theoretical results must be to a certain extent accidental; for no process of chemical analysis is capable of the accuracy which this agreement would imply. Still it should be noticed that the probable errors of the process, so far as they are indicated by the variations from the mean value, are not larger than we might expect would be eliminated by multiplying observations; and, further, that the mean of the last six determinations which are undoubtedly the most trustworthy, is nearly as close to the theory as the mean of the whole.

But not only did these experiments on bromide of antimony thus confirm our previous conclusion: they also gave the first definite clew to the explanation of the disagreement with otherwise consistent results which our experiments on chloride of antimony had presented. The one difference between the chloride and the bromide, which appeared to render the last better suited to yield accurate results, was the difference in their hygroscopic qualities. As we have stated, the chloride is one of the most hygroscopic substances known. The bromide is also hygroscopic, but far less so, presenting no unusual difficulties of manipulation; and, since our tests indicated that both substances were otherwise pure, we at once drew the inference that the different results we had obtained with chloride of antimony must depend on the extraordinary attraction of this substance for moisture. Before, however, fully following out the clew thus obtained, we made a similar study of the iodide of antimony.

The iodide of antimony was prepared like the bromide, by shaking up in a glass flask a solution of iodine in bisulphide of carbon with finely pulverized metallic antimony. On filtering and decanting, after the color of the iodine is discharged, a solution having a pale greenish-yellow color is obtained, from which on cooling or on evaporation red crystals of iodide of antimony are deposited. The substance may be purified by recrystallization from the same solvent; but iodide of antimony is far less soluble in bisulphide of carbon than the chloride or bromide, and cannot therefore be so advantageously treated in this way, nor can the small amount of carbonaceous impurity which the crystals acquire from the solvent be so easily removed. Moreover, iodide of antimony cannot be so readily distilled as the chloride or bromide, on account of its high boiling point, which is above that of metallic mercury. But another property of iodide of antimony which, so far as we know, has not hitherto been noticed, interferes still more seriously with these methods of purifying this substance. In all its conditions, it undergoes a more or less rapid oxidation in contact with atmospheric air, forming oxi-iodide of antimony ($SbOI$) and free iodine. When iodide of antimony is rapidly boiled in a small flask, so that the body and most of the neck are kept full of vapor at the boiling-point, the action at the surface of contact of the vapor and the air is very striking; iodine is set free in vapor, with its familiar violet color, while the oxi-iodide is precipitated in clouds, forming a most beautiful phenomenon. So also when the greenish-yellow solution (above described) of the iodide in bisulphide of carbon is exposed to the air and light, it rapidly becomes colored red from the liberation of iodine, and at the same time turbid from the deposition of the insoluble oxi-iodide. Even the crystals of iodide of antimony, when kept in the light, slowly become opaque from the formation of the same oxi-iodide; while the odor and staining of the stopper of the bottle furnish abundant proof of the liberation of iodine. The study of these phenomena was most interesting, and the results obtained will be described in another paper. It is sufficient for the present to say that they pointed out to us a great source of impurity in iodide of antimony, and fully explained the want of accordance in our analyses of the crystals of this substance as first prepared. It was evident that we could only hope to purify the material by distilling or subliming it in an atmosphere of inert gas; and we devised the apparatus represented in the accompanying figure for this purpose, which we have since found very generally useful for all sublimations where the temperature required does not exceed that which can be measured with a mercury thermometer. The apparatus has been already referred to (page 26), and requires no further description. It was a simple modification of the apparatus used before for drying at a regulated temperature the precipitates of sulphide of antimony, which, as we have stated, was so arranged that the character of any sublimates which might be given off could be observed. We used the same glass tube passing through the sheet-iron air-bath, with its transparent mica cover, only we added a common glass adapter, selected so that its mouth just fitted over the open end of the tube. A platinum nacelle containing iodide of antimony, which had already been purified by crystallization, was placed in the tube within the air-bath, but near the open mouth; and, while a current of dry carbonic dioxide through the apparatus was steadily maintained, the air-bath was heated by a gas lamp to the required temperature which was



indicated by a thermometer, as shown in our figure. Iodide of antimony is sensibly volatile, even at 100° ; and long before it reaches its melting point, 167°, the evaporation becomes very marked. As soon as melted, it sublimes quite rapidly ; and we obtained the best results by keeping the temperature between 180° and 200°, and, by shifting the adapters we used as receivers, it was easy to collect the different portions of the sublimate. We thus obtained crystals of two isomeric modifications of iodide of antimony: the more abundant in large hexagonal plates, often half an inch or more in diameter, perfectly transparent, and of the most brilliant ruby-red color; the other in small rhombic plates, having the same peculiar greenish-yellow color as the solution of the iodide already mentioned. The amount of the last was always small, but it was larger in proportion as the temperature was lower. This new and most interesting product will be described in the paper just referred to. Of these crystals, the most brilliant, chiefly of the red variety, were selected for analysis. The iodine determinations were conducted in all respects like those of chlorine and bromine. The iodide was first dissolved by a very concentrated solution of tartaric acid, and then the solution was diluted to the required extent. The same care was taken not to add more than a very slight excess of argentic nitrate, and the amount required was accurately weighed out in each case. Each of the determinations was made with a separate preparation in so far as it was a product of a separate sublimation; but the material sublimed was essentially the same in all cases, — a mixture of the products of many crystallizations from the crude material made as described above. The results are collected in the following table: —

Analysis of Iodide of Antimony.

Iodine Determinations.

No.	Wt. of SbI_3, grammes.	Wt. of AgI, grammes.	% of Iodine, I = 127, Ag = 108.	Variety.
1.	1.1877	1.6727	76.110	Pure red.
2.	0.4610	0.6497	76.161	Chiefly yellow.
3.	3.2527	4.5716	75.956	Pure red.
4.	1.8068	2.5389	75.939	Pure red.
5.	1.5970	2.2456	75.990	Red and yellow.
6.	2.3201	3.2645	76.040	Pure red.
7.	0.3496	0.4927	76.161	Chiefly yellow.

Mean value	76.051
Theory Sb = 120, requires . .	76.047
Theory Sb = 122, „ . .	75.744

If in calculating the results of these iodine determinations we use the atomic weights of Stas, I = 126.85 and Ag = 107.93, the mean value would be 76.034, and the corresponding atomic weight of antimony 119.95.

The difference (0.004) between the first mean value and theory — corresponding to only about $\frac{2}{10}$ of a milligramme in the largest amount of argentic iodide weighed — is evidently insignificant, so that these results confirm the lower value of the atomic weight of antimony as closely as did the analyses of the bromide.*

---

* After the success we had in the application of our method of sublimation to purifying the iodide, we attempted to purify the bromide of antimony in the same way. We thus obtained a very beautiful product, free from every trace of impurity except hygroscopic moisture. The last could not be avoided without more efficient means than we then had of drying the necessarily somewhat rapid gas current; but we were satisfied that with proper precautions, this would be a better method of preparing pure antimonious bromide than the one

As we have already intimated, our analyses of the iodide of antimony, as first crystallized from bisulphide of carbon, yielded very discordant results. These we give in the table below, not, as before, in the exact order in which the analyses were made, but in the order of the several values, so as to exhibit the distribution of the errors.

ANALYSES OF CRYSTALLIZED ANTIMONIOUS IODIDE, RED VARIETY.

No.	% of Iodine.
1.	75.71
2.	75.76
3.	75.78
4.	75.80
5.	75.84
6.	75.85
7.	75.87
8.	75.89
9.	75.94
Mean value	75.83
Theory $Sb = 122$	75.74
Theory $Sb = 120$	76.05

The cause of this discordance we attributed, as we have intimated, chiefly to the remarkable readiness with which iodide of antimony undergoes oxidation in contact with the air, resulting in the formation of oxi-iodide of antimony and free iodine, thus: —

$$2\,SbI_3 + O{=}O = 2\,SbOI + 2\,I{-}I.$$

While the free iodine escapes, the oxi-iodide remains as an impurity in the preparation, and the effect is a replacement of a portion of its iodine by oxygen. Now, since eight parts of oxygen replace one hundred and twenty-seven parts of iodine, it can readily be seen that an otherwise almost imperceptible amount of oxidation would be sufficient

---

we employed. For the reasons stated the results of the analyses of the preparations we made in this way were not as concordant as those exhibited on page 54, although the close agreement of the mean result with that above given was very striking, and in one analysis, using three and one-half grammes of carefully selected material, we obtained 66.662% Bromine.

to produce all the variation from the normal composition which the above results present. A simple calculation will show that an absorption of only $\frac{47}{1000}$ths of one per cent of oxygen, or less than half a milligramme by each gramme of iodide of antimony, would reduce the per cent of iodine from the theoretical value, 76.047, to the mean of the above results, 75.832; and that a corresponding absorption of three-quarters of a milligramme would reduce the per cent to 75.700, the lowest observed. It is not, therefore, surprising that we could obtain concordant results only with material which had been both purified by crystallization and also *recently* sublimed.

Returning now to discuss again the cause of the disagreement of the analyses of antimonious chloride with our otherwise consistent results in regard to the atomic weight of antimony, it was obvious that the strong hygroscopic power of the chloride must lead to a replacement precisely similar to that which is produced in the iodide by direct oxidation; for, as we have before said, the crystals of antimonious chloride cannot be exposed to the atmosphere for an instant without absorbing a perceptible amount of moisture, and every molecule of water thus absorbed reacts on a molecule of the chloride, thus: —

$$SbCl_3 + H_2O = SbOCl + 2\,HCl.$$

And when the antimonious chloride is boiled, the hydrochloric acid formed is given off, while the oxichloride remains behind, dissolved in the great mass of the liquid. Indeed, it seems impossible, with our ordinary appliances, to prepare or purify antimonious chloride without its becoming contaminated with oxichloride; and our experiments would indicate that when once it has been formed, as above described, in the mass of the material, it cannot be wholly removed by distillation or crystallization, however often these processes may be repeated.

Naturally, our attention was very early called to this obvious source of impurity in the antimonious chloride we prepared; and we noticed from the first that, even after the material had been many times distilled, there was always left, on repeating the process, a very small amount of dark-colored residue. We had examined the residue, and found that it was a mixture of chloride and oxichloride of antimony, colored by a trace of carbonaceous material; and we had made a long series of analyses for the purpose of studying the effect produced by the action we have described. The result of these analyses is given in the following table. We started with material already purified by fractional distillation and crystallization, and distilled it ten times in succession; not, however, carrying the distillation to absolute dryness, but leaving, so far as we could judge by the eye, about the same amount of residue in the retort each time. These residues we analyzed, as we did also the final distillate. The material first distilled was the same as that marked *c* in the table on page 40, and we assumed that the average of the results there given truly represented its composition.

ANALYSES OF ANTIMONIOUS CHLORIDE.

RESIDUES AND DISTILLATES.

	% of Chlorine.
The original purified preparation	46.64
The residue of 1st distillate	45.71
„ 2d „	45.66
„ 3d „	46.03
„ 4th „	46.26
„ 5th „	46.26
„ 6th „	46.00
„ 7th „	46.03
„ 8th „	45.94
„ 9th „	45.65
„ 10th „	45.99
The last distillate	46.62

Although, under the circumstances, we could not expect great precision, yet it was evident from these analyses that the amount of impurity in the residues was not diminished by the successive distillations; and we therefore concluded that additional oxichloride of antimony must be formed each time during the very short contact with the atmosphere which the transfers between the several distillations necessarily involved. But, on the other hand, the very remarkable fact that these ten distillations produced no sensible change in the composition of the great mass of the material seemed to indicate equally clearly that this action of the atmosphere had no perceptible influence on the final result; and this opinion was still further strengthened when, on twice distilling portions of the last distillate, at a low temperature, in a current of dry hydrogen, we obtained products giving again — very nearly at least — the same per cent of chlorine. And, lastly, when to all this evidence were added the results of the complete analysis of the chloride, showing an amount of antimony which fully supplemented the very constant per cent of chlorine, the assumption that any material amount of impurity could be present appeared wholly untenable. Yet we have seen how this assumption was forced back upon us by the subsequent results of the investigation.

Returning to the subject after our experiments with iodide of antimony, we, for the first time, fully appreciated how very small an amount of oxygen — the only real impurity present — was required to reduce the per cent of chlorine in antimonious chloride from 47.02, the amount corresponding to $Sb = 120$, to 46.61, which corresponds to $Sb = 122$; for, while the effect is so differently produced, yet the result of the action of the atmosphere on the chloride of antimony is wholly like that of its action on the iodide. It ends in replacing a small amount of chlorine by oxygen; and although, in consequence of the smaller atomic weight of chlorine, it requires in this last case a larger replacement to produce a corresponding change of percentage composition, yet still the amount required to make all the difference in question is very small; so that, when we come to sum up the supposed completed results (as on page 42), it might easily be covered up by slight inaccuracies of the analytical work. An easy calculation will show that the substitution of but $\frac{146}{1000}$ of one per cent of oxygen for the equivalent amount of chlorine would reduce the per cent of this last element in the chloride from 47.020, corresponding to $Sb = 120$, to 46.608, which corresponds to $Sb = 122$; and such a substitution would result from the absorption of only $1\frac{6}{10}$ milligrammes of water by each gramme of the chloride. The composition of the material would then be as follows: —

Composition of Antimonious Chloride with $\frac{146}{1000}$ % of O when $Cl = 35.5$ and $Sb = 120$.

Chlorine	46.608
Oxygen	.146
Antimony	53.246
	100.000

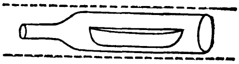
Now it will be seen by referring to the tables, on pages 40 and 42, that these percentages do not differ from the mean of the results of our previous analyses as much as these results differ among themselves; and we therefore determined to repeat these analyses, hoping that the experience we had acquired in both chlorine and antimony determinations would now enable us to obtain results sufficiently sharp to show even the small differences of composition which the substitution in question would produce.

Meanwhile, we instituted a series of experiments with a view of studying the decomposition which the oxichloride of antimony undergoes under the action of heat, in the hope that we might thus discover some method by which the amount of oxichloride of antimony in our preparations might be directly determined. For this purpose, we used first crystallized $SbOCl$, obtained by the action of alcohol on chloride of antimony in a sealed tube, which we weighed out into a platinum nacelle, and heated to various regulated temperatures, using for this purpose the apparatus already described. It appeared that the decomposition took place in two stages. The first stage of the decomposition began between 167° and 175°, but was not completed until between 260° and 280°. The second stage began at about 320°, but required for its completion a red heat. During both stages, chloride of antimony sublimed; and there was left in the nacelle at the close of the process beautiful crystals of Sb_2O_3. In another experiment, we used crystallized $Sb_4O_5Cl_2$, prepared in the same way as the $SbOCl$, but with different proportions of alcohol and chloride of antimony. In this case, the decomposition did not begin until 320°, but in other respects both the process and the products were as in the first experiment. It was quite evident that the chemical changes which took place in the two stages of decomposition we have noticed were represented by the following reactions: —

First stage: $5\,SbOCl = Sb_4O_5Cl_2 + SbCl_3$; (1)

Second stage: $3\,Sb_4O_5Cl_2 = 5\,Sb_2O_3 + 2\,SbCl_3$; (2)

but the relative weights observed in the first two experiments were of no value, because it was evident that a no inconsiderable amount of Sb_2O_3 was lost by sublimation. Since, however, the small sublimate of oxide condensed in the glass combustion-tube very much nearer the nacelle than the very much larger sublimate of chloride, we varied the apparatus in our third experiment so far as to place the nacelle in a tube of the shape represented in the accompanying figure.



This tube was weighed with the nacelle, and was so selected that it quite closely fitted the combustion-tube within which it was placed for heating, as shown in figure by dotted lines. And it is evident that, while with this arrangement the $SbCl_3$ would be swept by the CO_2 gas into the colder portion of the combustion-tube, the greater part at least of the sublimed oxide would be retained in the small tube, which was of course at each stage weighed with the nacelle as at first. Our results were as follows: —

Weight of SbOCl	0.4939	grammes.
Loss at 280°	0.1271	„
Required by theory of reaction 1, if Sb = 120	0.1305	„
Total loss at red heat; that is, in both stages .	0.2179	„
Required by theory of reactions 1 and 2 . .	0.2174	„

It was evident from this determination that the order of the decomposition was precisely that indicated by our reactions, although the end of the first stage was not quite so sharply marked as the end of the second; and this would naturally be expected.

As the residues obtained on distilling chloride of antimony showed, when further heated, precisely the same order of phenomena which we have just described, and when heated to redness yielded the same crystals of oxide of antimony as before, it was plain that the residue left on evaporating the chloride at a temperature not exceeding 120° was chiefly at least SbOCl; but that this when heated more intensely was converted into $Sb_4O_5Cl_2$ before the temperature reached 280°, and finally at a red heat was converted wholly into Sb_2O_3. We therefore endeavored to determine the amount of oxichloride in one of our preparations of chloride of antimony by distilling a weighed amount from a platinum nacelle at as low a temperature as possible in a current of dry carbonic acid, and heating the residue to a temperature of about 275°. We thus obtained the following results: —

No.	Wt. of $SbCl_3$.	Residue.	% of Residue $Sb_4O_5Cl_2$.
1.	6.7286	0.0212	0.315
2.	4.5150	0.0151	0.334
3.	7.9320	0.0258	0.325

In order to yield 0.146 % of oxygen, which would reduce the per cent of chlorine in the preparation from 47.020 to 46.608, as in the scheme on page 62, there would be required 1.155 % of $Sb_4O_5Cl_2$.

Although the results of the above determinations accord within a few per cent of the quantity estimated, yet it was perfectly clear during the course of the experiments that they did not at all represent the total quantity of the oxichloride present in the preparation examined. Not only was the composition of the preparation not materially altered by the slow distillation, — a fact shown by the determinations marked *e* in the table on page 40, and by which we were misled at the outset, — but also the product from our distillation yielded when distilled again apparently as much residue as before. In a word, we found the same phenomena repeated in these distillations at a low temperature which had been so noticeable when the chloride was distilled at its boiling point, and which are so strikingly illustrated by the results given on page 61. It is possible, as before suggested, that the effects might arise from a small additional absorption of water at the successive transfers which the repeated distillations involved; or, in the later experiments, from the circumstance that the very extensive apparatus employed for drying the carbonic dioxide was not completely effectual. Still, now that our attention had been called to the danger, and we had taken unusual precautions on both these points, the explanations suggested did not seem to us sufficient; and we came to the conclusion that the oxichloride must distil over with the chloride of antimony to a certain limited extent, and that it was only an excess above this definite amount which was left behind as residue. Of course, SbOCl not only is not volatile, but is at once decomposed by heat; and we do not suppose that this compound by the tension of its own vapor is carried over in distillation. It is a very dilute solution, as it were, of SbOCl in $SbCl_3$ which thus distils; and the distillation of the oxichloride may resemble the carrying over of boracic acid by the vapor of water, and similar phenomena, the result, as it is has always appeared to us, of a feeble kind of chemical union which has been usually designated by the term "molecular combination." Such a theory would account for the remarkable constancy which we have found in the chlorine determinations of the various preparations of antimonious chloride purified by distillation. But, on account of the very great difficulty of removing all possible disturbing causes, we found it impossible to obtain a rigid experimental demonstration of our theory without much more time and labor than we could then command. We hope to return to the subject hereafter. Meanwhile, however, it was evident that we could place no reliance whatever on the results just obtained. Nevertheless, the determinations were of value on account of the contrast between these results and those of a similar series of experiments on the residues from antimonious bromide which we collect in the following table: —

No.	Wt. of $SbBr_3$.	Residue chiefly $Sb_4O_5Br_2$.	% of residue.
1.	2.8342	0.0010	0.035
2.	2.0220	0.0006	0.030
3.	4.6730	0.0010	0.021

As will be seen, this residue is less than one-tenth of that obtained from the chloride, and is practically insignificant. Evidently, then, in the determination of the atomic weight of antimony more accurate results may be expected from the analysis of the bromide than from the analysis of either the chloride or the iodide of this element. The intermediate position of the bromide renders it, in a very remarkable way, the most stable of the three compounds. It absorbs moisture far less eagerly than the chloride, and it absorbs oxygen far less readily than the iodide, and is thus in great measure protected against each of these two sources of the same impurity.

We come finally to the new analyses of antimonious chloride we had undertaken. Fortunately, some of the old preparation that had been distilled so often had been preserved. It had been boiled for a long time since the last analyses were made, and kept in the same flask used for determining its boiling point, which had stood meanwhile tightly corked in a desiccator over sulphuric acid. The solid mass in the flask was easily broken up without exposure to the air by simply heating it to the melting point, and shaking it in the flask as soon as, beginning to melt, the mass had separated from the glass. Near its melting point, chloride of antimony becomes very friable, and is thus easily reduced to coarse powder, whence probably the old alchemistic name of butter of antimony. It is also worthy of notice that neither the bromide nor the iodide acts in this way, as we found out in more than one instance to our cost.

Thus we were readily able to prepare our material for analysis, and, by a thorough mixing of the mass, to insure that the several samples taken had a uniform composition. In regard to the antimony determination, no further details are necessary. It was conducted, as described before, with every minute precaution which experience had suggested; and we give the full details, in order to show how completely we had been able to overcome the difficulties which it at first presented, and we feel confident that there is no process of wet analysis which is capable of giving more accurate results than this.

Details of Antimony Determination.

The antimonious chloride was first transferred to a very carefully dried weighing tube, and thence to the large flask in which it was dissolved. The transfer to the weighing tube was made in a dry atmosphere, and only required two or three seconds. It is evident, however, that a slight absorption of moisture at this point is not important; for, even if it increased the apparent weight of the assay by several milligrammes, it would only reduce to a barely perceptible extent the percentages of all the constituents leaving the relative values wholly unchanged. It is only when, on boiling the chloride, after such an absorption, the chlorine is driven off, that the essential change of composition results.

Weight of tube and antimonious chloride	20.9609	grammes.
„ „ after transfer to flask	16.3920	„
„ chloride analyzed	4.5689	„

The weight of the tube and chloride while on the balance pan remained invariable for a sufficient length of time to give positive assurance of the constancy of the weights. The chloride was dissolved in a saturated solution of tartaric acid containing about 15 grammes of the pure acid, and then diluted with carbonic acid water and precipitated as before described. The precipitate, having been washed and collected as before, was dried in an air bath, at about 110°.

Weight of small filter	0.0434	grammes.
„ porcelain crucible	101.2132	„
	101.2566	„
„ crucible and precipitate	104.6762	„
„ red sulphide of antimony	3.4196	„

A portion of the dried precipitate dissolved in hydrochloric acid gave no residue. The rest was then transferred to a platinum nacelle, and heated, as has been described, in a current of dry carbonic dioxide gas. No sublimate was formed, and only a very slight empyreumatic odor could be perceived.

Weight of platinum nacelle	6.2493	grammes.
„ nacelle and dried precipitate . . .	9.5273	„
„ portion taken	3.2780	„
„ nacelle and precipitate after heating to 285° for over half an hour .	9.5234	„
Loss of weight of portion taken	0.0039	grammes.
Corresponding loss for whole precipitate . .	0.0041	„
Weight of red sulphide as above	3.4196	„
„ gray sulphide	3.4155	

The carbonaceous residue left on dissolving this whole amount of gray sulphide in hydrochloric acid was barely perceptible. It was collected, however, as usual, on a weighed paper disk, and estimated.

Weight of small paper filter	0.0198	grammes.
„ same with residue	0.0212	„
„ residue	0.0014	„
Calculated for whole precipitate	0.0015	„
Weight of gray sulphide as above	3.4155	„
Total weight of gray sulphide	3.4140	„
Corresponding weight of antimony assumed to be $\frac{5}{7}$ of the sulphide	2.4386	„
Per cent of antimony in the antimonious chloride under examination	53.374	„

It will be noticed that this result is practically identical with the mean of the previous determinations, which, as will be seen by reference to the table on page 42, was 53.401; and, by reviewing the facts stated in that connection, it will be perceived that this agreement is in itself alone a strong confirmation of the conclusion which we deduced from our first experiments on the synthesis of the gray sulphide of antimony, — that of the two values of the atomic weight of antimony in question, the lower is the more exact.

Coming next to the chlorine determinations, we noticed, for the first time, an effect which, under certain circumstances, may have an important influence on the accuracy of this well-known process, as employed in the analysis of chloride of antimony. In a precipitate of argentic chloride that had been deposited from an unusually concentrated solution of antimonious chloride in tartaric acid, and had stood over night, our attention was called to some crystalline grains, which, on examination, proved to be a compound of tartaric acid, antimony, and silver. We soon found that this product could be readily obtained by concentrating the filtrate from the precipitate of argentic chloride, and adding to it, while still warm, an excess of argentic nitrate. On cooling, the new crystals form in abundance. They have not yet been measured, but under the microscope they have the general aspect of right rhombic plates or prisms, with hemihedral modifications, — a general form which is so characteristic of the tartrates, and which we ourselves have previously studied in our crystallographic determinations of the tartrates of rabidium and cæsium.* We obtained for the amount of silver in the crystals, as a mean of three analyses, 26.30 per cent. The compound $Ag,SbO,H_2{\equiv}O_4{\equiv}(C_4H_2O_2) . H_2O$ would require 26.34 %. The crystals may therefore be regarded as tartar emetic, in which the potassium has been replaced by silver; and they resemble the crystals of this well-known salt in general form. They are evidently the same substance obtained by Wallquist† by precipitating nitrate of silver with tartar emetic, and analyzed both by him and by Dumas and Piria. These chemists obtained respectively 27.31 and 28.05 per cent of oxide of silver, which corresponds with the result given above as closely as could be expected; but they appear to have prepared the substance only in an amorphous condition. At least, in the description quoted, no mention is made of any crystalline form.

These crystals of argento-antimonious tartrate are apparently not acted upon in the least by cold water, and only slightly by boiling water; and finding this very insoluble material mixed with the precipitated chloride of silver, under the conditions stated, we were led to fear that it might be occluded to some extent by this precipitate, even when formed in much more dilute solutions of antimony and tartaric acid. The phenomenon was very similar to that we had already studied in the occlusion of the oxichloride by the sulphide of antimony; and there was reason to fear that, as in the previous case, an ŏcclusion of this double tartrate might result, even when the substance would not otherwise be precipitated. How far such an action could have vitiated our previous results, it was, of course, now impossible to determine; but, as we previously stated, we had always taken great care not to add more than the slightest possible excess of argentic nitrate, and this was especially true in our more recent determinations. Now, however, we were on our guard, and in the following determinations very great pains were taken to add just the requisite amount of the silver salt, and the argentic chloride was subsequently examined for traces of any such occlusion. But, excepting this close attention to well-known precautions, the determinations were made in the same way as before.

---

* Am. Jour. of Science and Arts. (2), xxxvii. 70.

† Gmelin Handbook, Cavendish Edition, x. 326.

ANALYSIS OF ANTIMONIOUS CHLORIDE.

No.	Wt. of $SbCl_3$.	Wt. of AgCl.	% of Chlorine.
1.	2.2220	4.1682	46.407
2.	1.9458	3.6512	46.420
Mean value			46.413

Bringing now the results together, — estimating the amount of oxygen by difference, as is usual in chemical analysis, and calculating what would be the composition of a preparation of antimonious chloride in which $\frac{213}{1000}$ of a per cent of oxygen had replaced an equivalent amount of chlorine, assuming, of course, $Sb = 120$ and $Cl = 35.5$, — we obtain the following very striking accordance: —

	Analysis.	Theory. $Sb = 120$, $Cl = 35.5$.
Chlorine	46.413	46.418
Oxygen	.213	.213
Antimony	53.374	53.369
	100.000	100.000

The general conclusions, then, which we deduce as the results of this investigation, are —

First, that the value of the atomic weight of antimony found by Schneider in 1856 — $Sb = 120.3$ — must be accurate within a few tenths of a unit, but that the most probable value of this constant, as deduced from our experiments, is $Sb = 120$, when $S = 32$.

Secondly, that the apparent disagreement with this result, presented by the partial analyses of antimonious chloride, is *probably* due to the constant presence of oxichloride in the preparations of this compound.

The investigation from the first has been a study of constant errors; and those who have followed us through the details will certainly allow that the opinions expressed at the beginning of this paper (on page 9) were not hastily conceived, even if they do not fully agree with our conclusions. In the attempts to correct or balance such errors, we have found at once the chief difficulties and interest of our work, and the secondary results thus reached seem to us the most important fruit of the whole investigation. Seeing, then, the sources of constant error we have discovered, and knowing that there are others whose influence we have been able to trace, although we have not been able to define them as clearly as we could desire, it would be presumptuous in us to express too great confidence either in the correctness of our theories or even in the conclusiveness of our experimental results. Of this, however, we feel assured, that more trustworthy results cannot be expected from a repetition of the same processes until a more complete and accurate knowledge has been acquired of the substances employed. We have therefore proposed to ourselves a more thorough investigation of the haloid compounds of antimony, and the first results of this investigation we shall shortly publish. After the requisite data have been thus collected, we hope to return to the old problem with such definite knowledge of the relations involved as will enable us to obtain at once more sharp and decisive results than are now possible.

During the course of this investigation, we have been successively aided in the experimental work by Dr. F. A. Gooch, Mr. C. Richardson, and Mr. W. H. Melville, at the time students in this laboratory; and without their assistance we could not have accomplished the great amount of labor it involved.

HARVARD COLLEGE LABORATORY, *June 12th*, 1877.